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Introduction to Ion Chromatography

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LIVE WEBCAST

Thursday 29th Nov. 2012, 11:00 AM EST; 15:00 GMT; 16:00 BST

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Outline

- Basic Theory of Ion Chromatography
- Columns
  - Ion Exchange Process
  - Altering Selectivity with buffers and column choice
- Detection and Suppression
  - Basic concept
  - State of the Art
- Modern Day Ion Chromatography
  - Concept and schematics of new Systems
  - Fast Ion Chromatography
  - Capillary Ion Chromatography
  - IC MS

Difficulties associated with the measurement of small ionic species using liquid chromatography

- No retention on traditional reverse phase columns for separation
- Mostly no UV absorbance for detection
- Ion exchange eluents for separation give too high a background to use conductivity as a means of detection

History of Ion Chromatography (IC)

Early 1970s:

Ion chromatography (IC) was developed by Hamish Small and co-workers at Dow Chemical Company as a novel method of IEC usable in automated analysis.

The Dow Chemical Company technology was acquired by Durrum Instrument Corp., which later formed a separate business unit for its new IC products, naming it **Dionex** (**D**ow **Ion Ex**change).

Ion chromatography (IC) is a process that allows the separation of ions and polar molecules based on their charge properties. Detection of the separated ions is usually achieved with conductivity detection.

Ion Chromatography Analytes

Functional groups detected with suppressed conductivity

Suppressed conductivity detection

Carboxylics

R–C(=O)–OH

Sulfates

R–O–S(=O)(=O)–OH

Sulfonates

R–S(=O)(=O)–OH

Phosphates

R–O–P(=O)(OH)–OH

Phosphonates

R–P(=O)(OH)–OH

1° Amines

$R-NH_2$

2° Amines

R–N(R′)–H

3° Amines

R–N(R′)–R″

4° Amines

R_4N^+

Inorganic Anions

e.g., F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, I^-, Br^-, ClO_3^-, SCN^-, $S_2O_3^{2-}$

Inorganic Cations

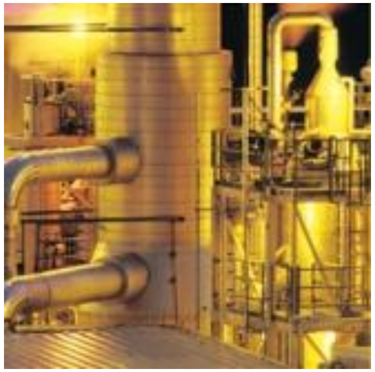
Alkali Metals: Li^+, Na^+, K^+, Rb^+, Cs^+

Alkaline Earths: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}

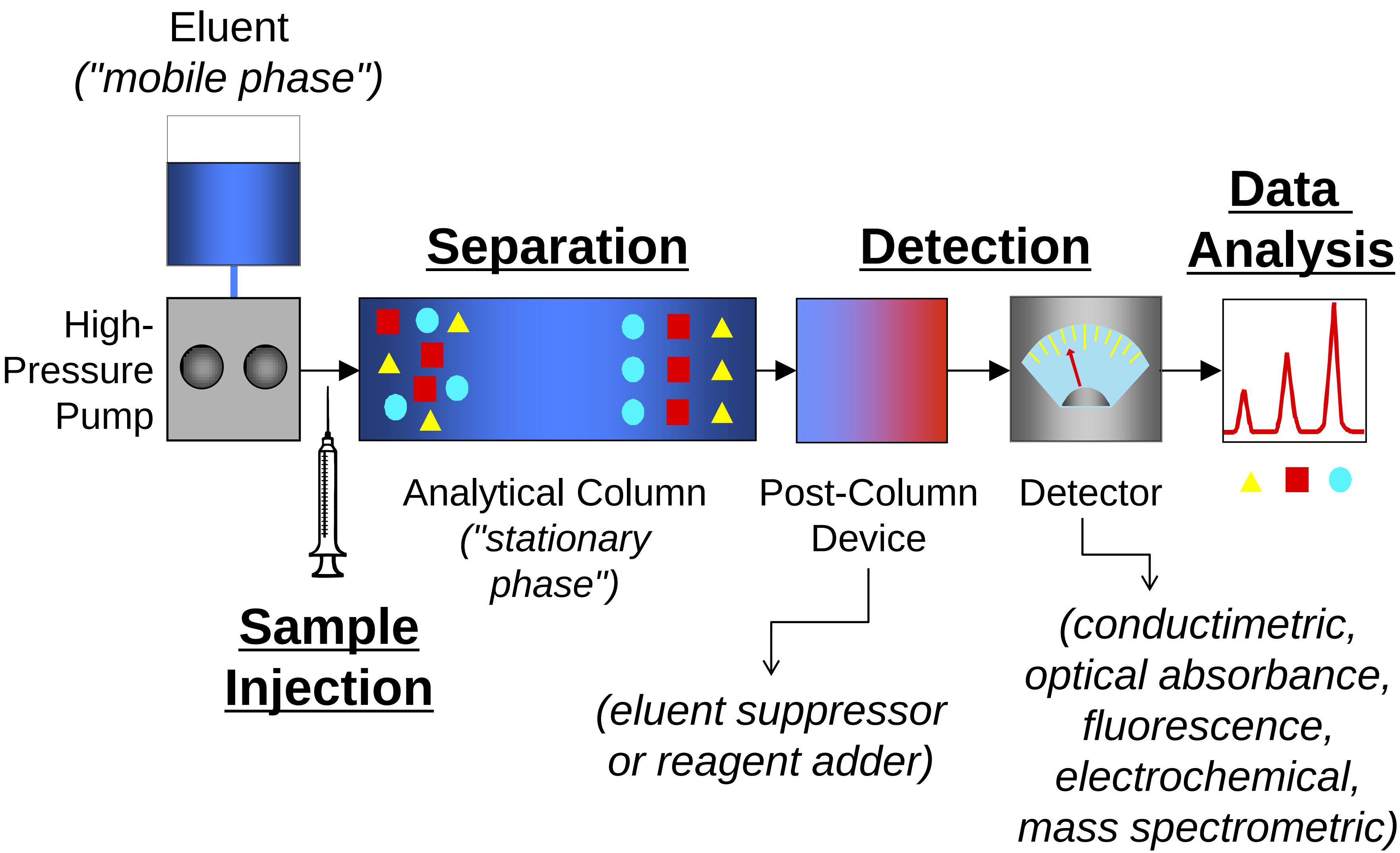
Ammonia: NH_4^+

Who uses Ion Chromatography (IC)?

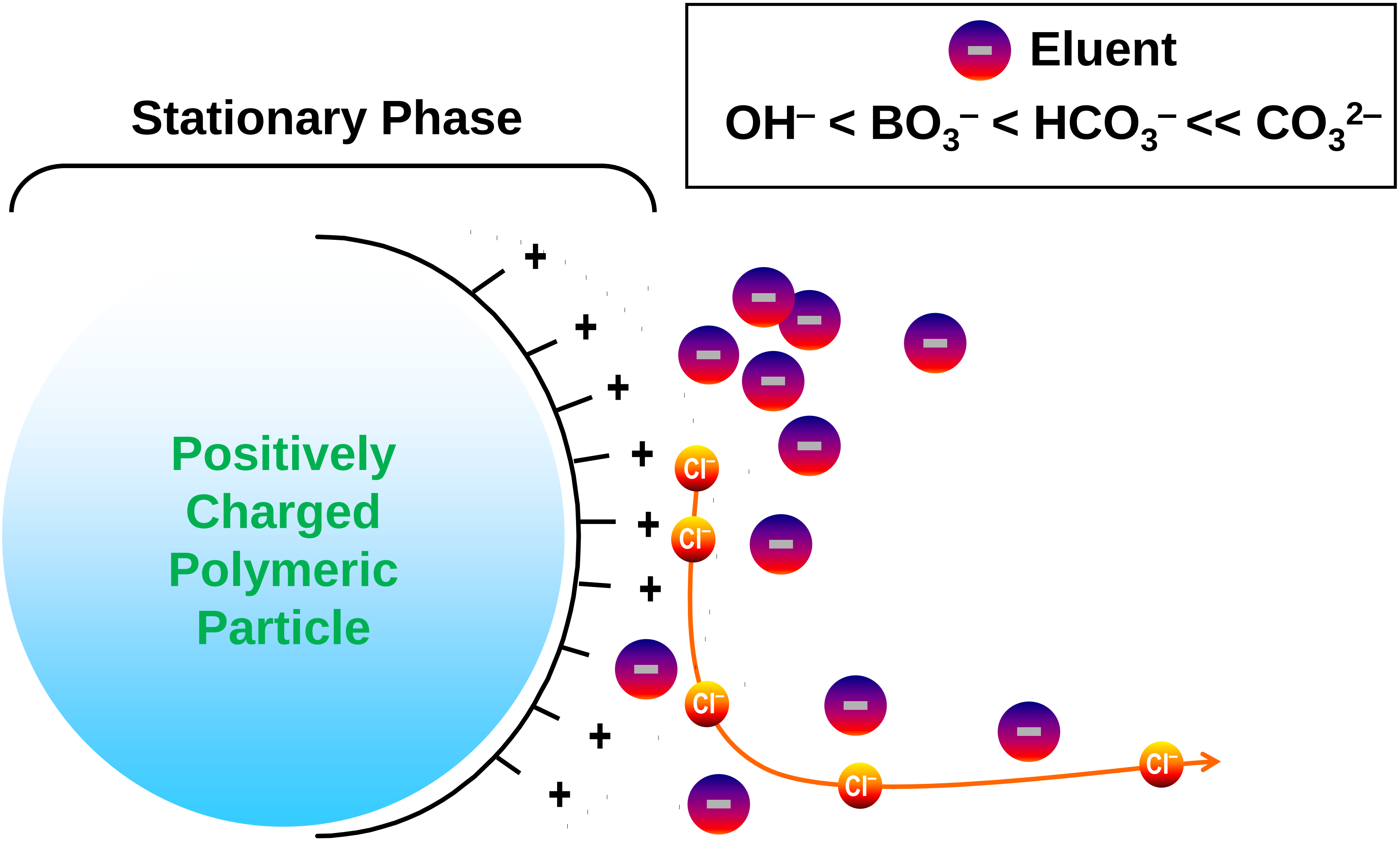
- Environmental Testing Labs
- Water providers
- Wastewater treatment facilities
- Pharmaceutical companies
- Chemical/petrochemical companies
- Food producers and processors
- Power utilities
- Electronics manufacturers
- Mining/metals/plating companies
- Government agencies
- Universities
- and more…

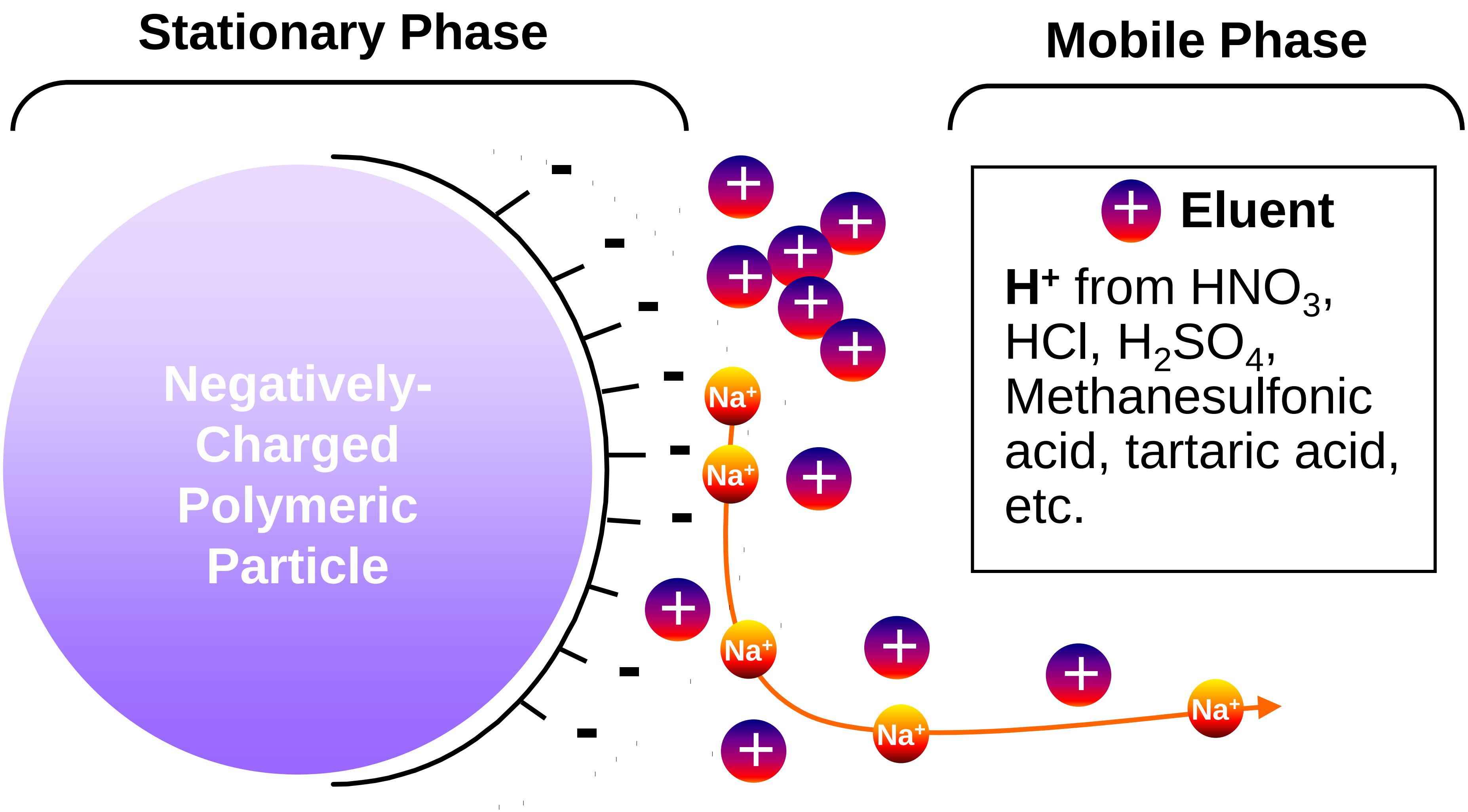
How does Ion Chromatography work?



The Ion Exchange Process

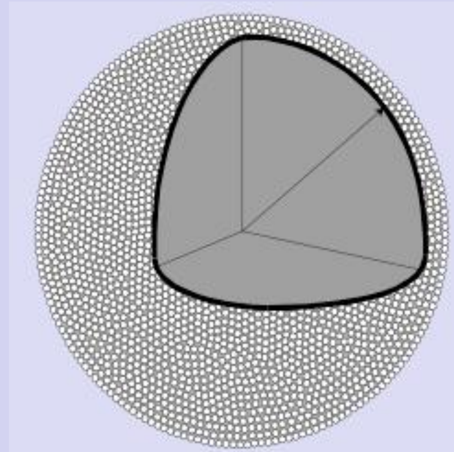


The Cation Exchange Mechanism



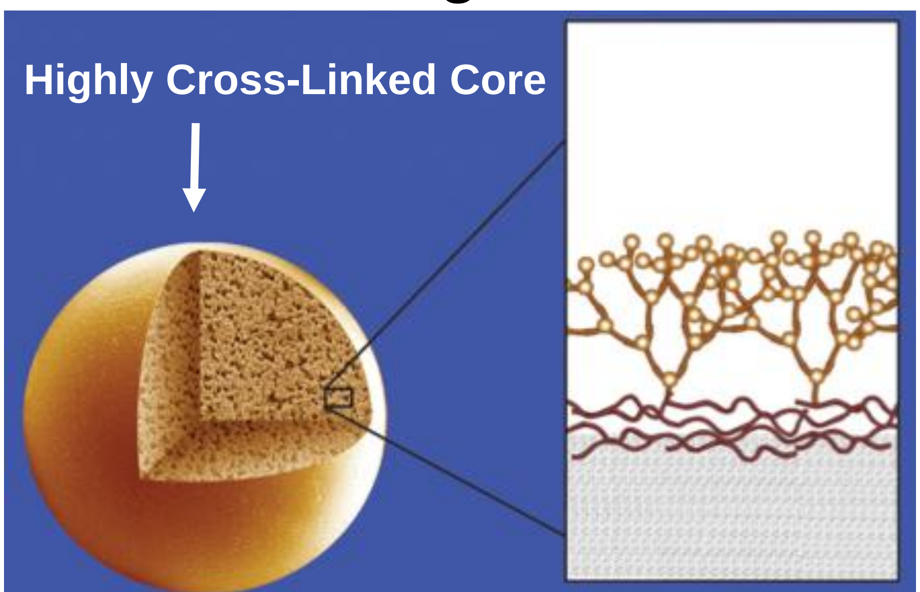
Examples of Column Chemistries

Latex agglomerated Anion Exchanger

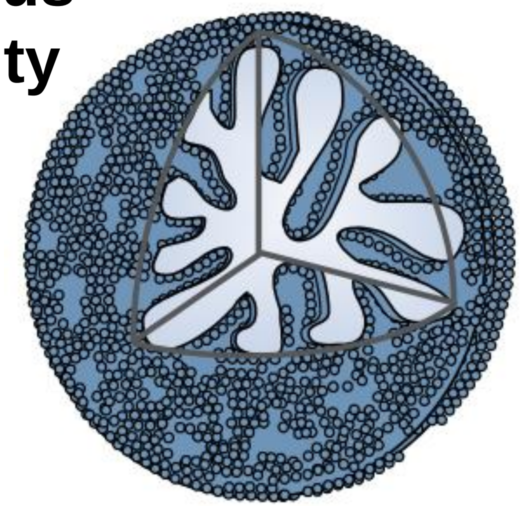


- Cross-Linked EVB-DVB core
- 5-10 µm diameter particles
- NanoBead™ anion-exchange layer

Hyper-Branched Surface Modified Anion Exchanger



Macro porous high capacity Anion Exchanger



Three factors that will affect resolution:

- ✓ Efficiency
- ✓ Capacity
- ✓ Selectivity

Altering Selectivity in Ion Chromatography

- Mobile phase parameters
  - Eluent Ion
  - Eluent concentration
  - Eluent pH
  - Organic additives
  - Temperature

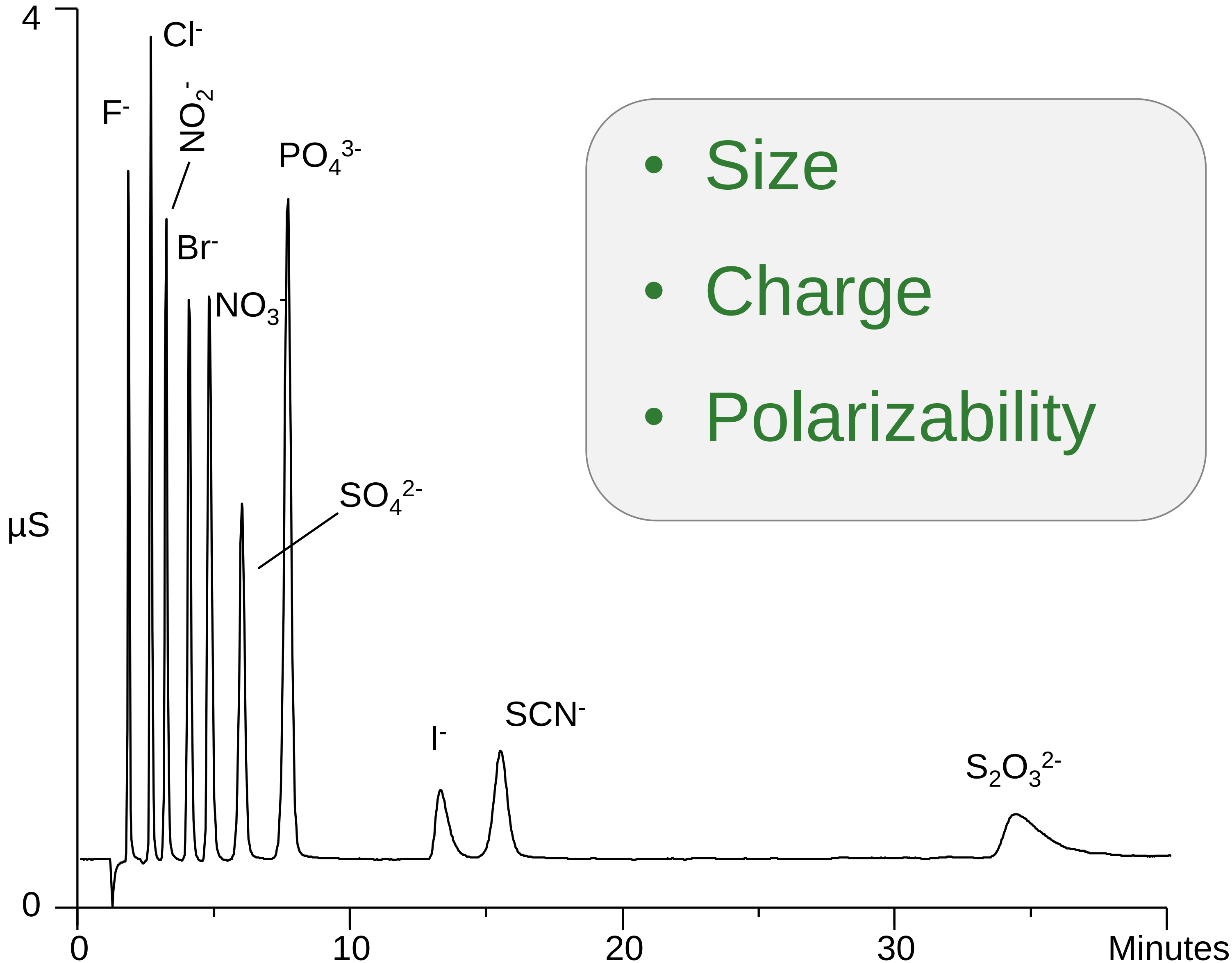
Mainly **retention** changes.

Little control on **selectivity**

- Stationary phase parameters
  - Material
  - Functional group
  - Capacity

Better control of **selectivity**

Parameters Controlling Ion Exchange Retention

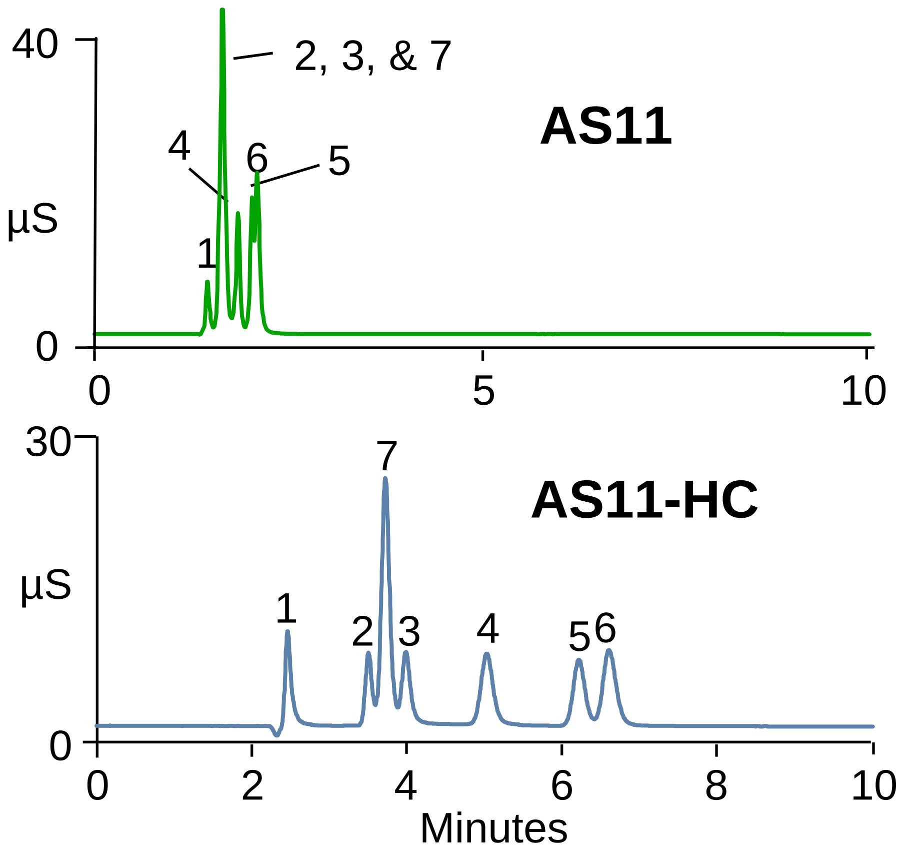


- Size
- Charge
- Polarizability

Effect of Stationary Phase Capacity

Number of ion exchange sites/weight equivalent of column packing.

The higher the capacity, the stronger the retention.



- Most ion exchange column have low capacity to improve detection and sensitivity
- Complex samples and measurement of trace levels in the presence of high level matrix ions require higher capacities

Peaks:

1. Fluoride 2. Chloride 3. Nitrite

4. Phosphate 5. Bromide 6. Nitrate 7. Sulfate

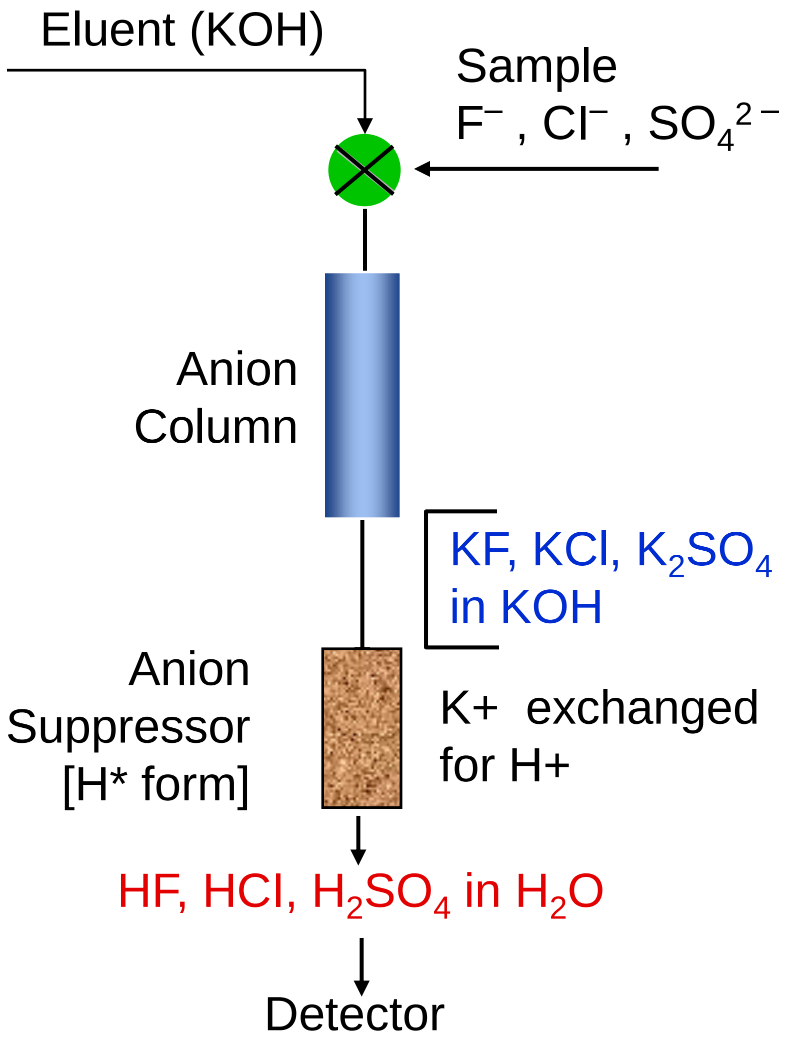
Suppression Theory

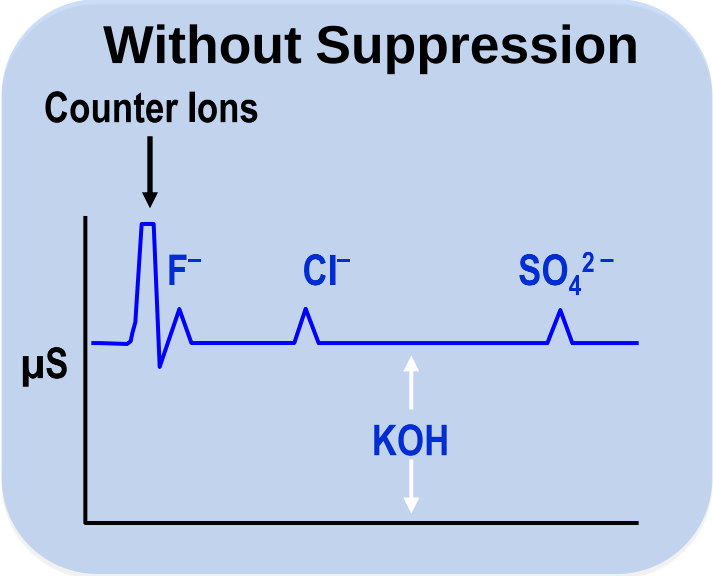
- ✓ Suppression is defined as the neutralization by ion exchange of the salt of a weak acid or weak base eluent.
- ✓ Two results of suppression are:
  - ✓ Decreases background conductivity
  - ✓ Increases analyte response

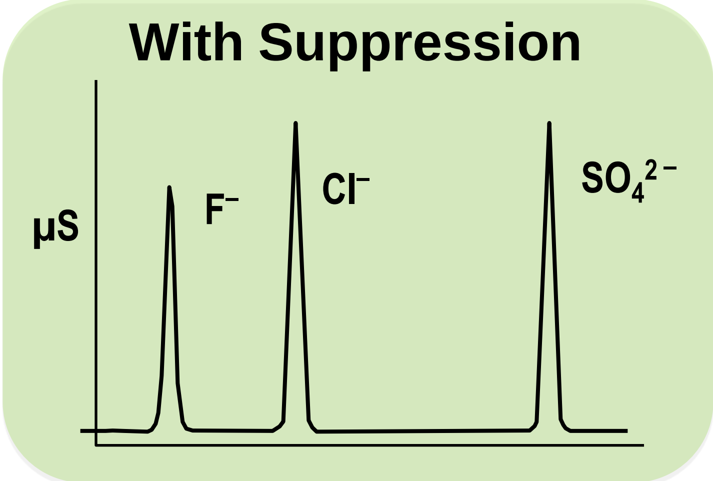
Suppressed Conductivity Detection

- Batch Suppression
- Continuous Suppression

Batch Suppression with Conductivity Detection

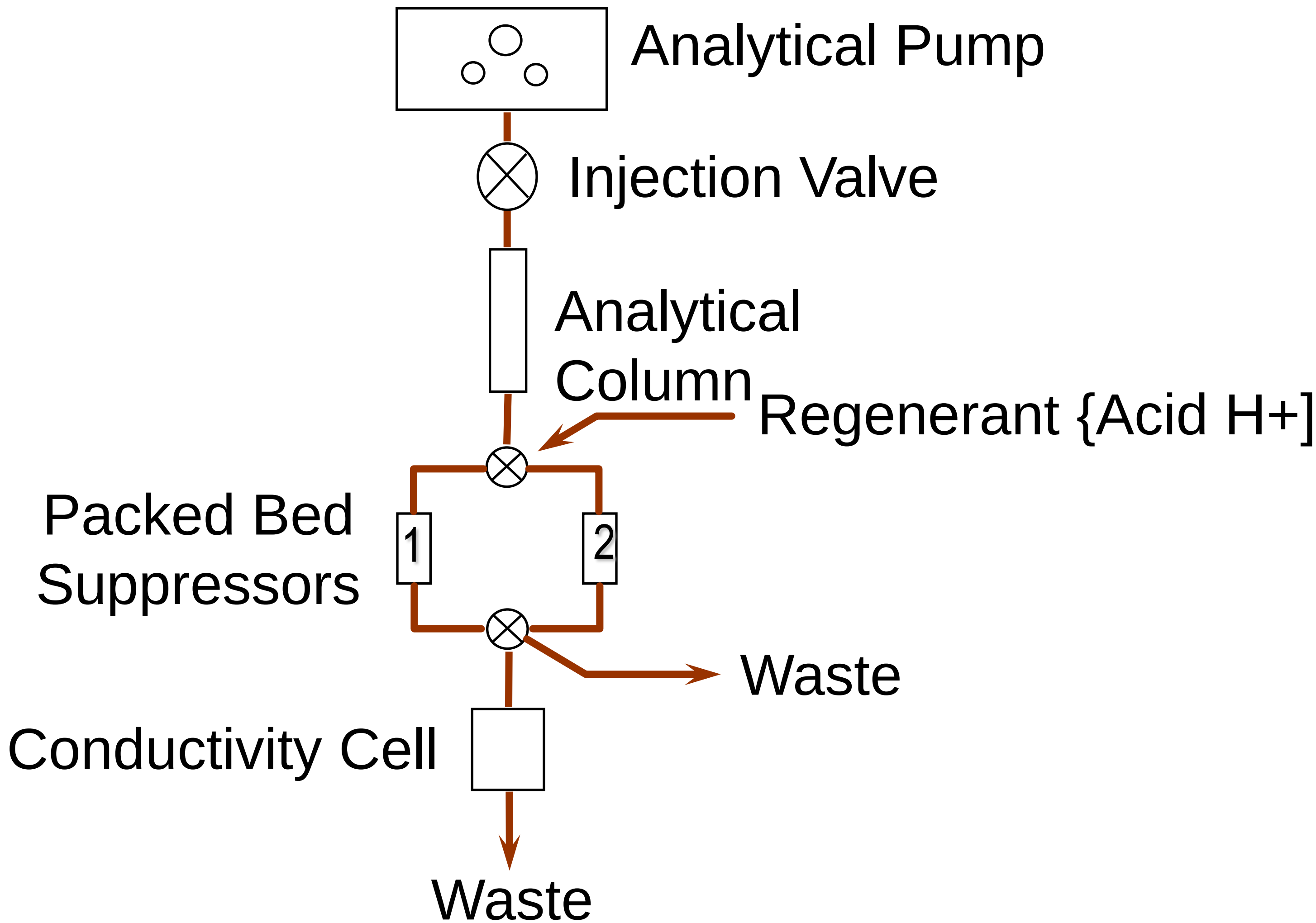






Problem – Capacity and Dead Volume!

Batch-Mode Suppressor Configuration



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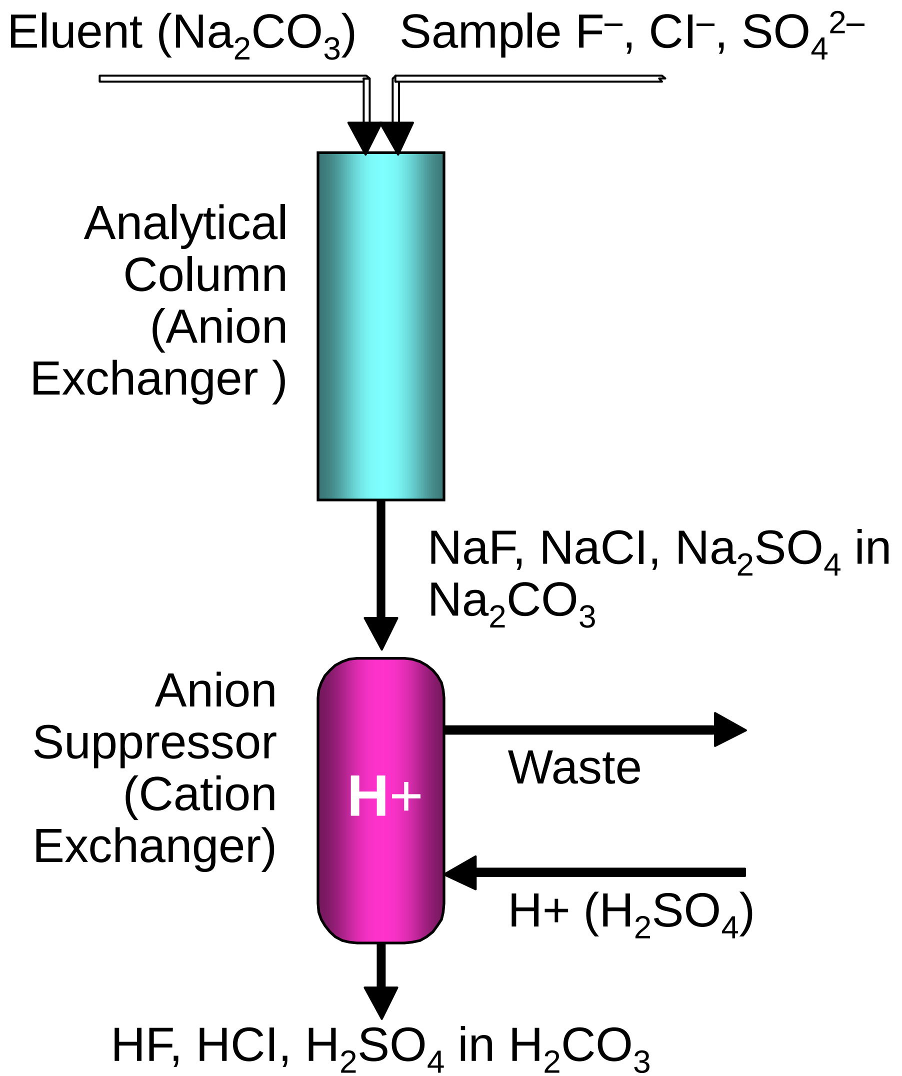
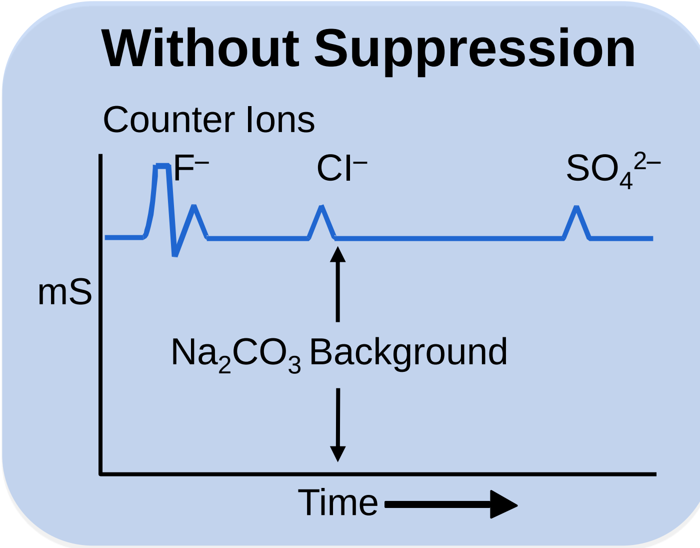
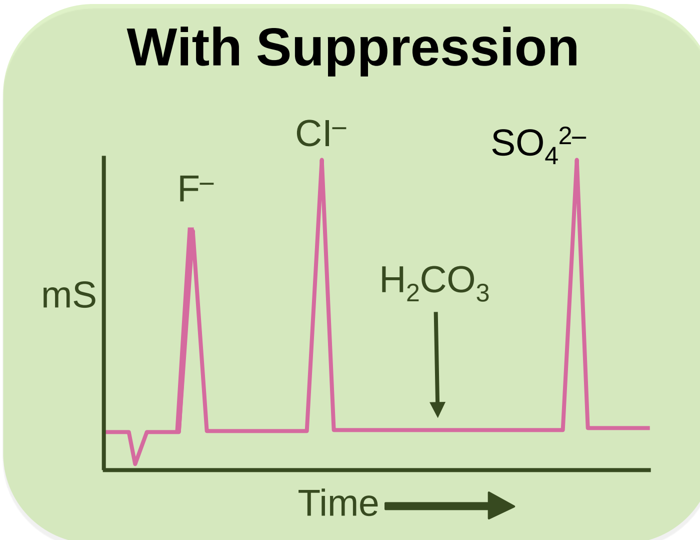
Continuous Chemical Suppression

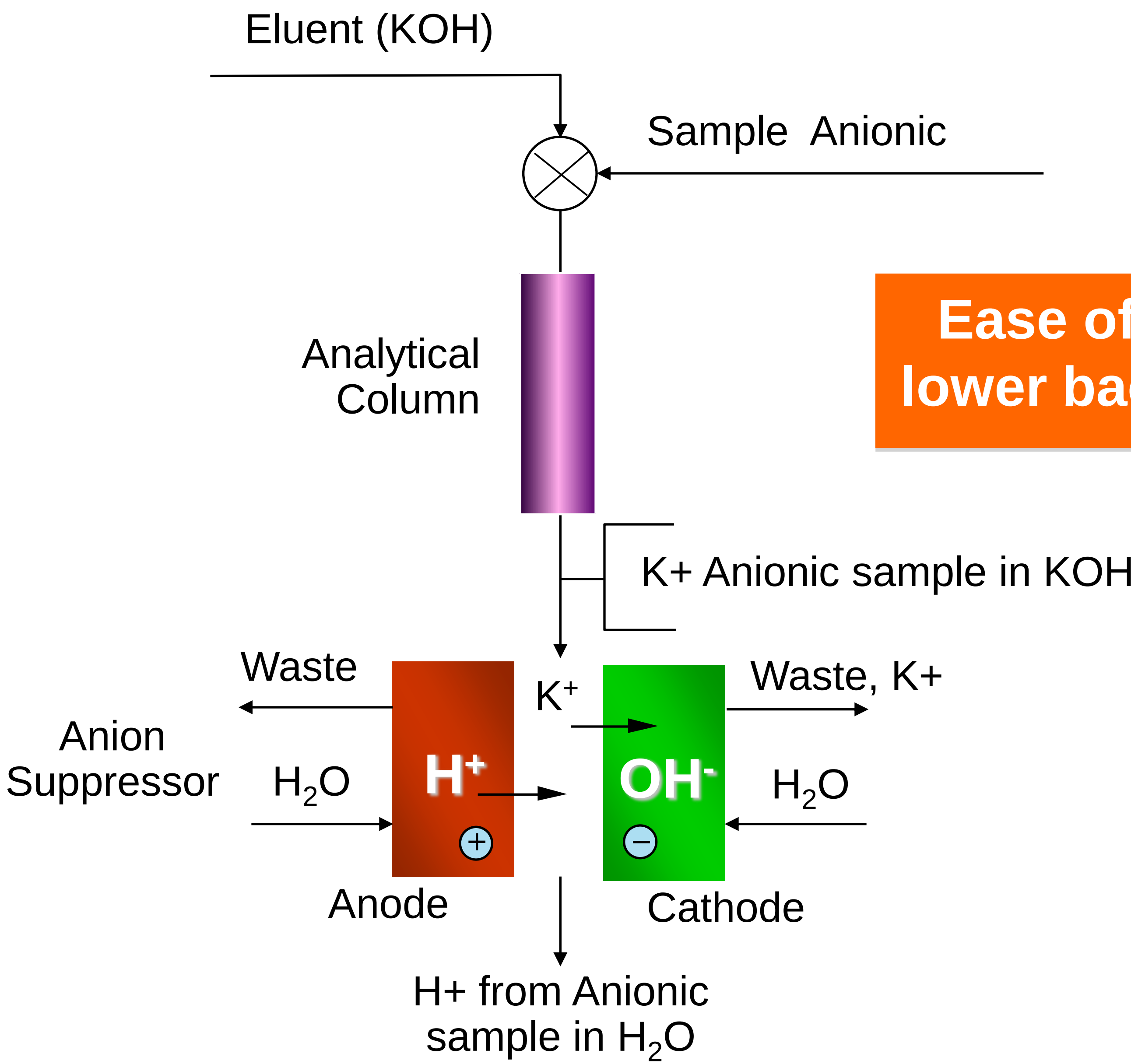






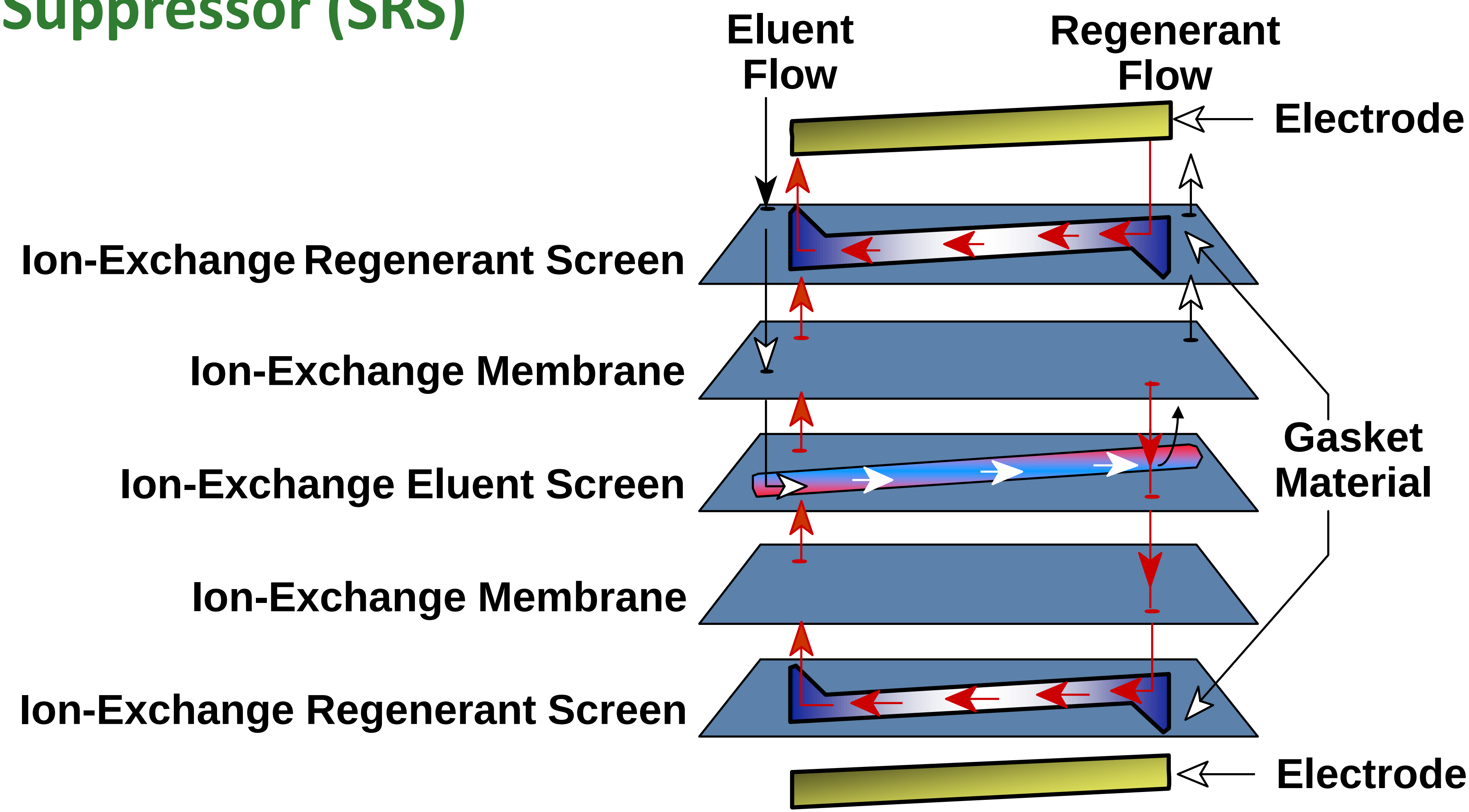
Continuous and low dead volume

Electronic Suppression



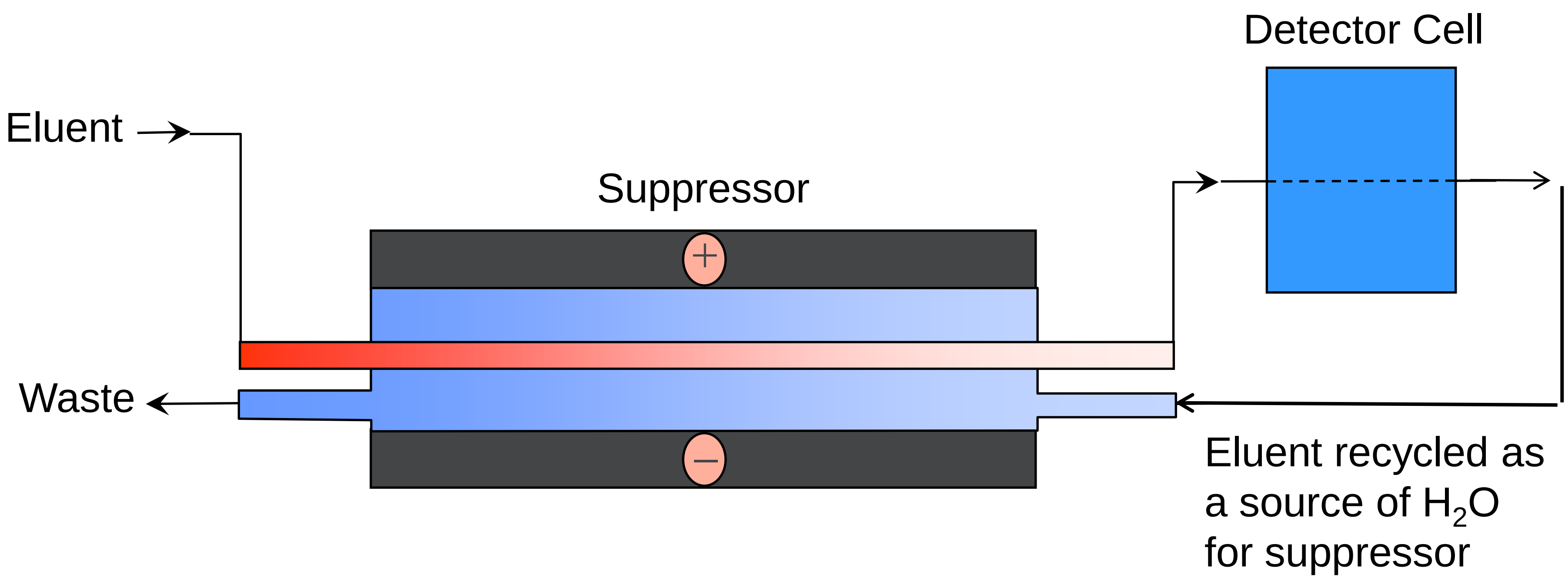
Ease of use with lower backgrounds

Design of a Self Regenerating, Continuous Suppressor (SRS)



High Capacity with very small delay volumes

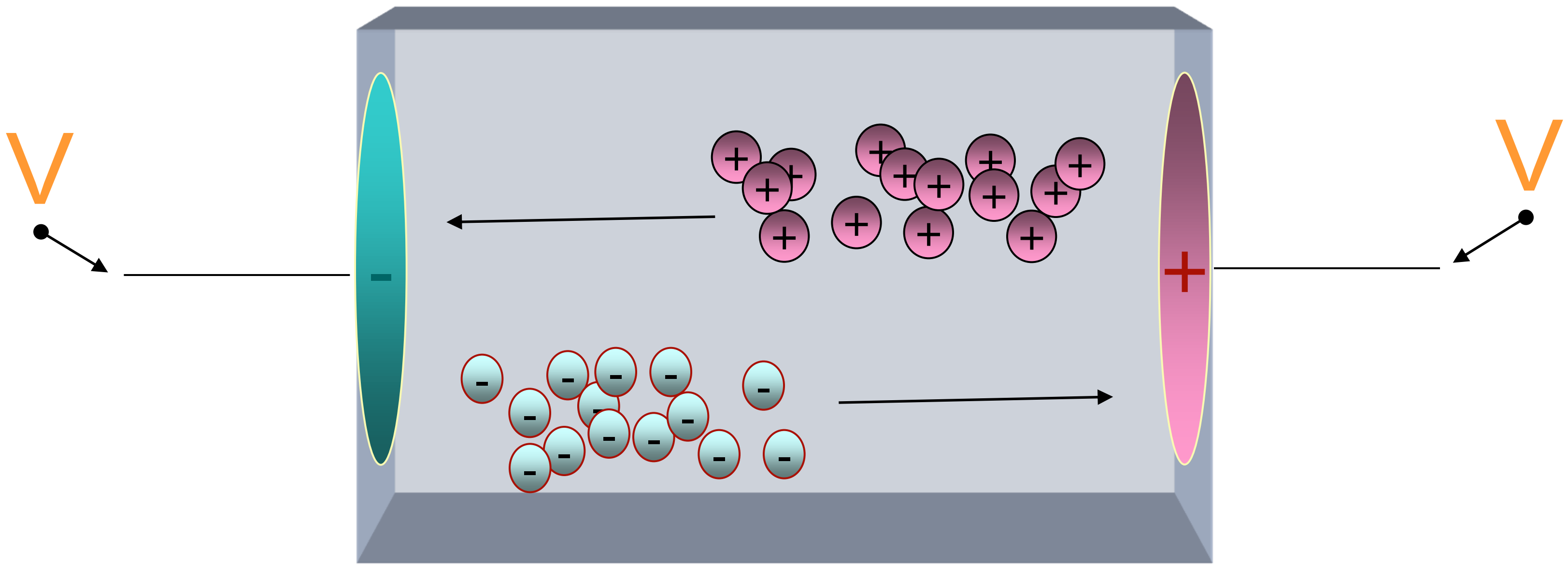
SRS® Ultra II AutoSuppression® Recycle Mode



Benefits of Continuous Suppression and the Important Link to Column Choice

- Larger Dynamic Working Range – High Sample load
- Allows the use of high capacity ion exchange columns
  - Use of high ionic strength mobile phases
- Allows the use of Gradient-Elution and higher resolution in combination with conductivity detection
- Coupling Ion Chromatography with other Detectors (e.g. MS, ICP-MS)

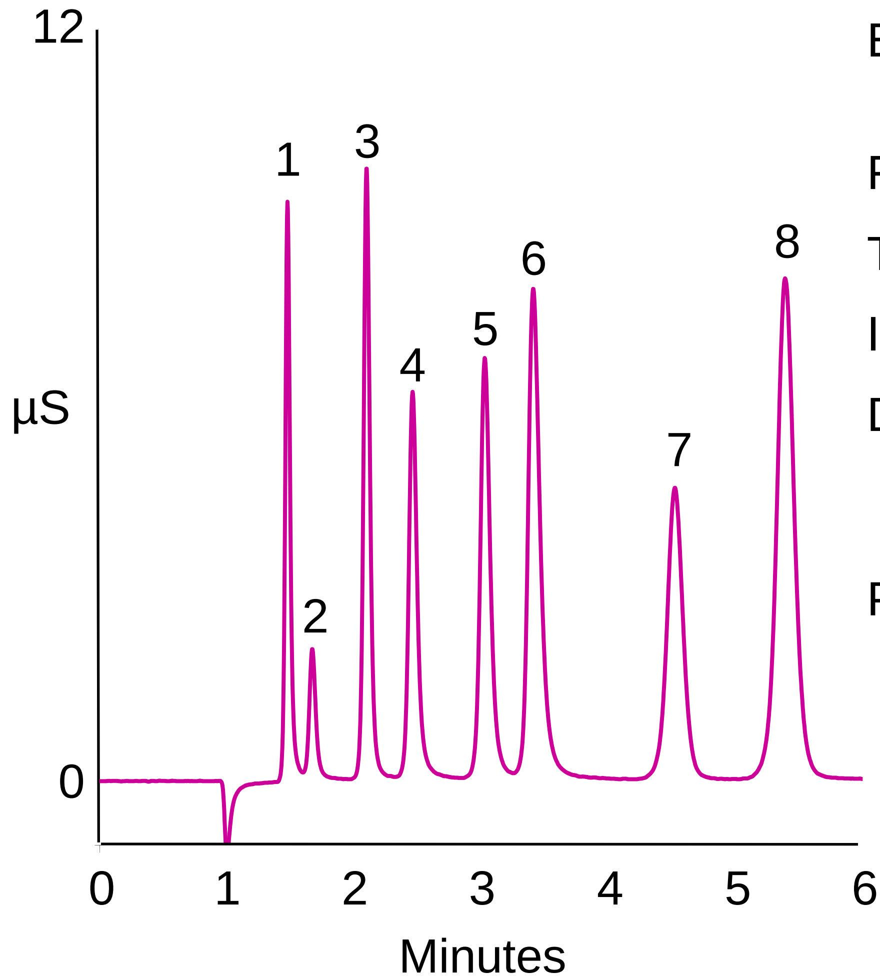
How is Conductivity Measured?



The conductivity of a solution is measured by applying an alternating voltage between two electrodes in a conductivity cell.

At any instant in time, negatively charged anions migrate toward the positive electrode and positively charged cations migrate toward the negative electrode.

Isocratic Anion Separation

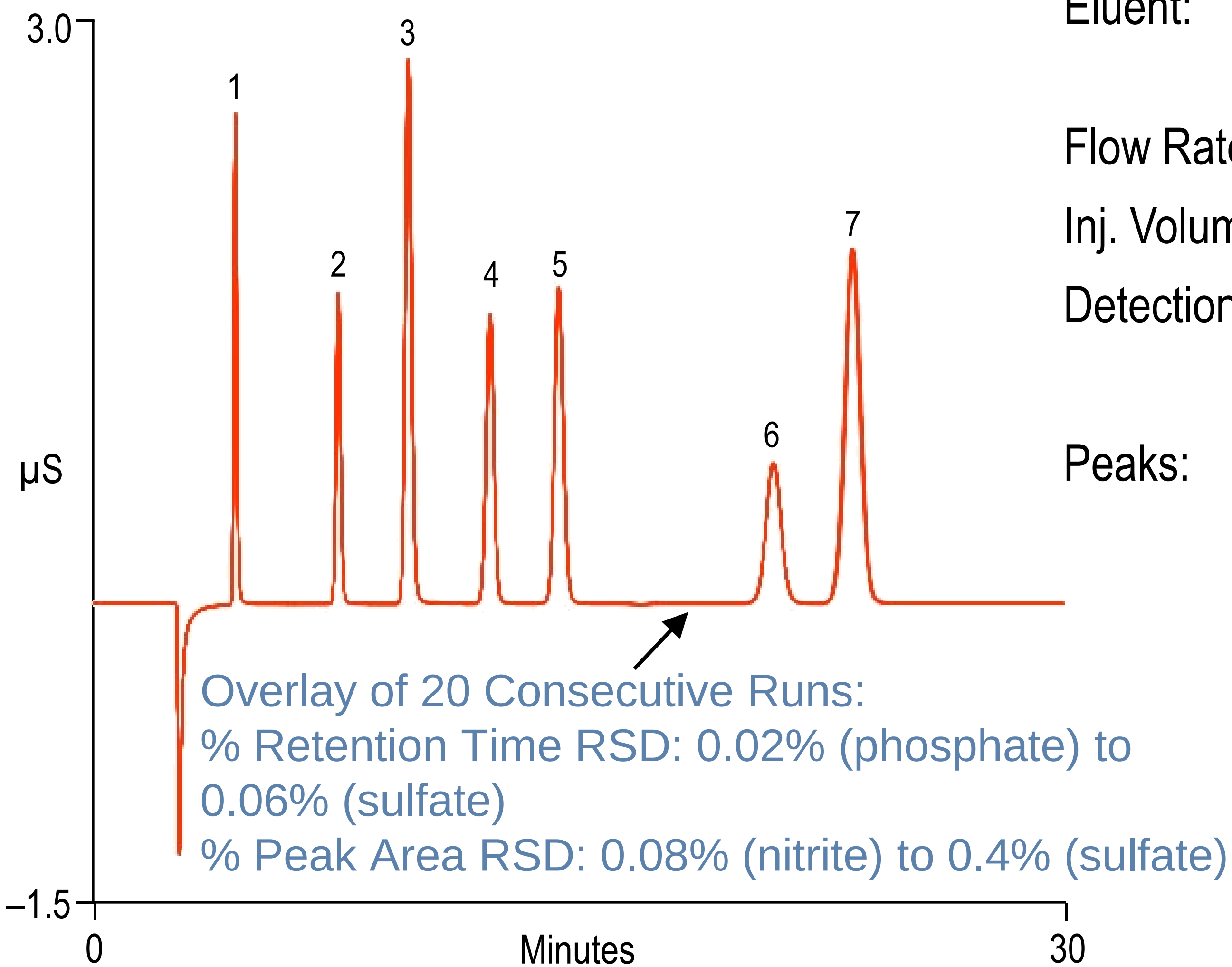


Column:	IonPac® AG14A, AS14A, 5µm, 3 x 150 mm
Eluent:	8.0 mM sodium carbonate 1.0 mM sodium bicarbonate
Flow Rate:	0.8 mL/min
Temperature:	30 ° C
Inj. Volume:	5 µL
Detection:	Suppressed conductivity, ASRS® ULTRA II, 2 mm, AutoSuppression® recycle mode

Peaks:

1. Fluoride	5mg/L (ppm)
2. Acetate	20
3. Chloride	10
4. Nitrite	15
5. Bromide	25
6. Nitrate	25
7. Phosphate	40
8. Sulfate	30

Reproducibility of Common Anions on AS23 Column



Column: IonPac AS23, 4 × 250 mm

Eluent: 4.5 mM Na_2CO_3
0.8 mM $NaHCO_3$

Flow Rate: 1.0 mL/min

Inj. Volume: 25 µL

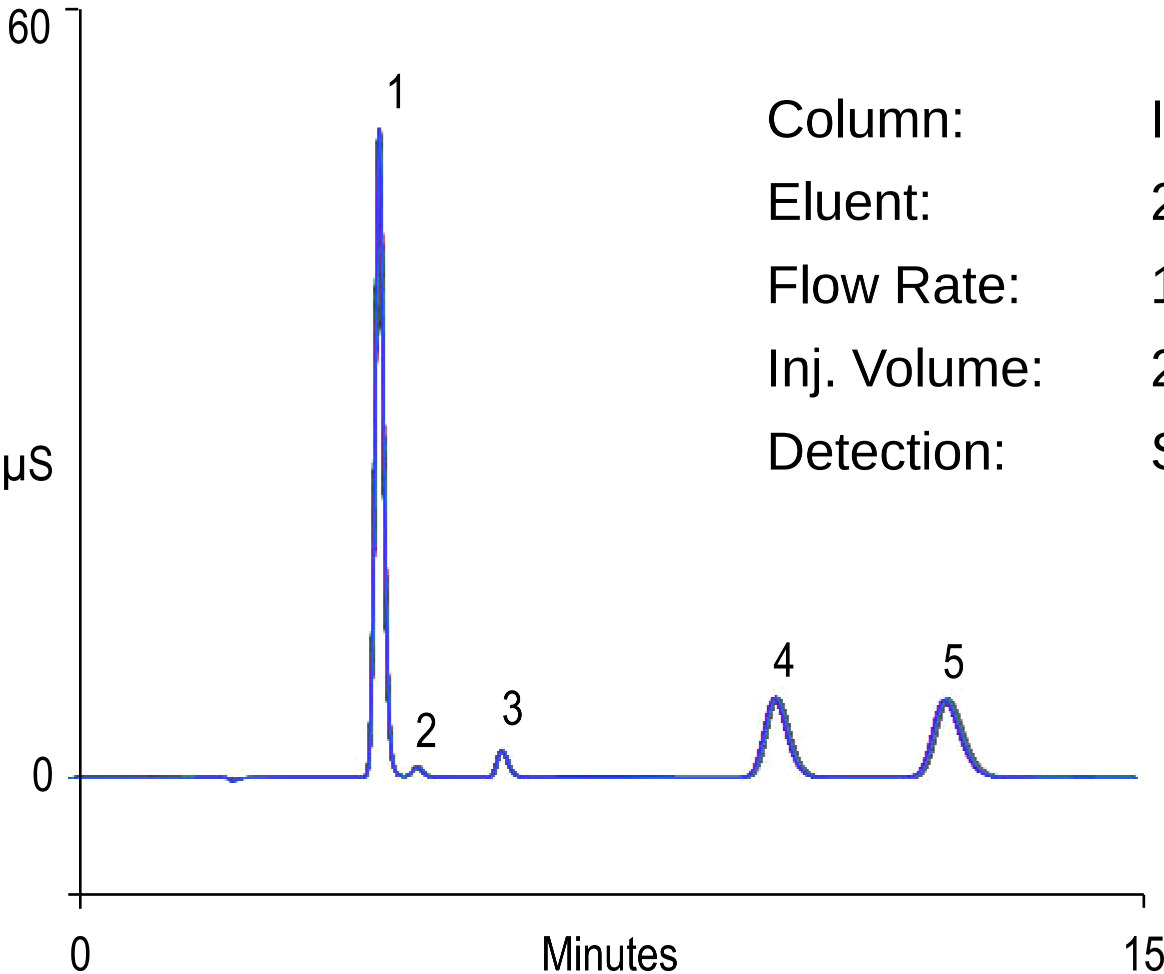
Detection: Suppressed conductivity

Peaks:

1. Fluoride	1.0 mg/L
2. Chloride	1.5
3. Nitrite	5.0
4. Bromide	5.0
5. Nitrate	5.0
6. Phosphate	7.5
7. Sulfate	7.5

Reproducibility of Common Cations in Drinking Water

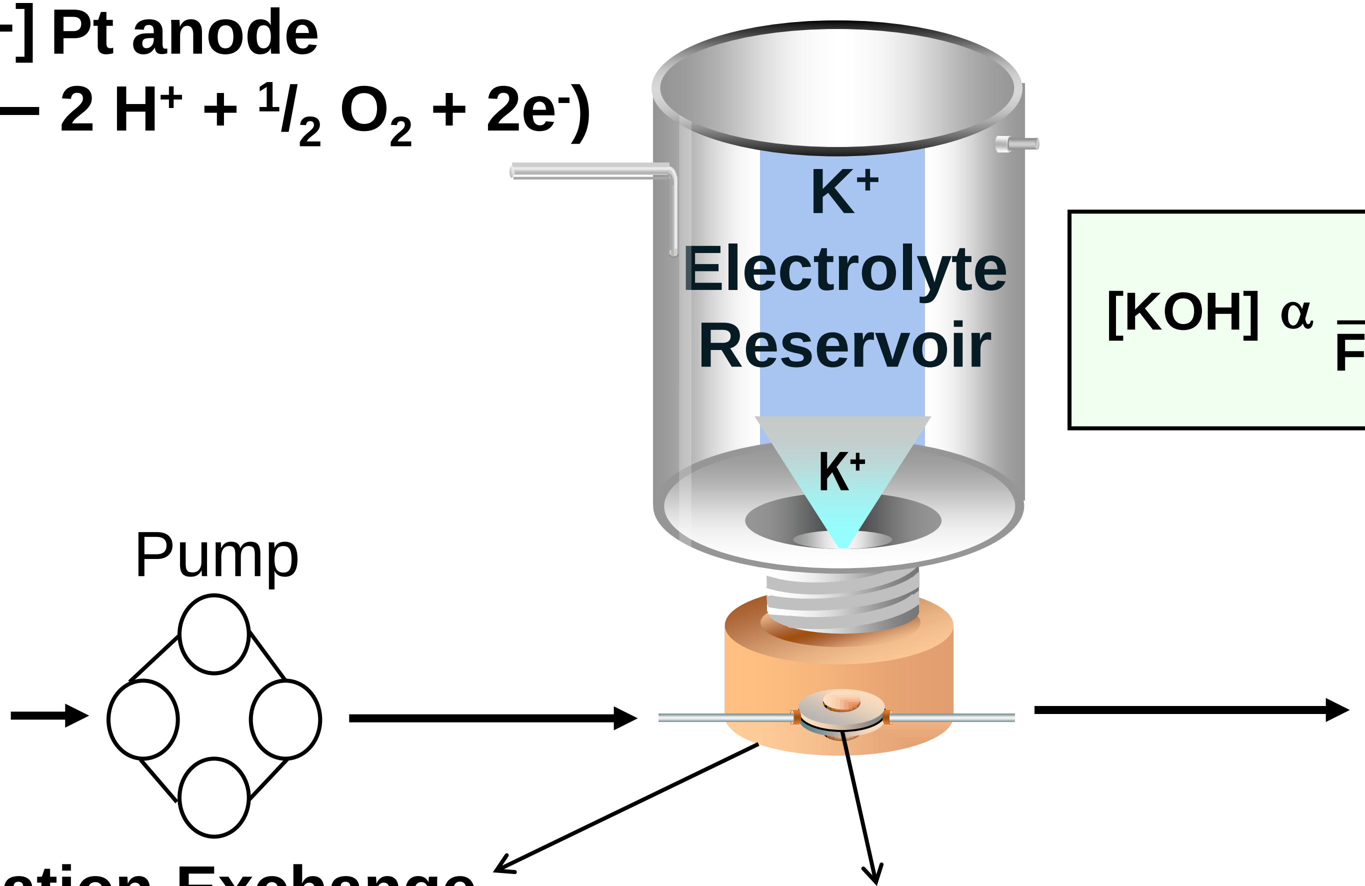
Overlay of 300 Consecutive Runs



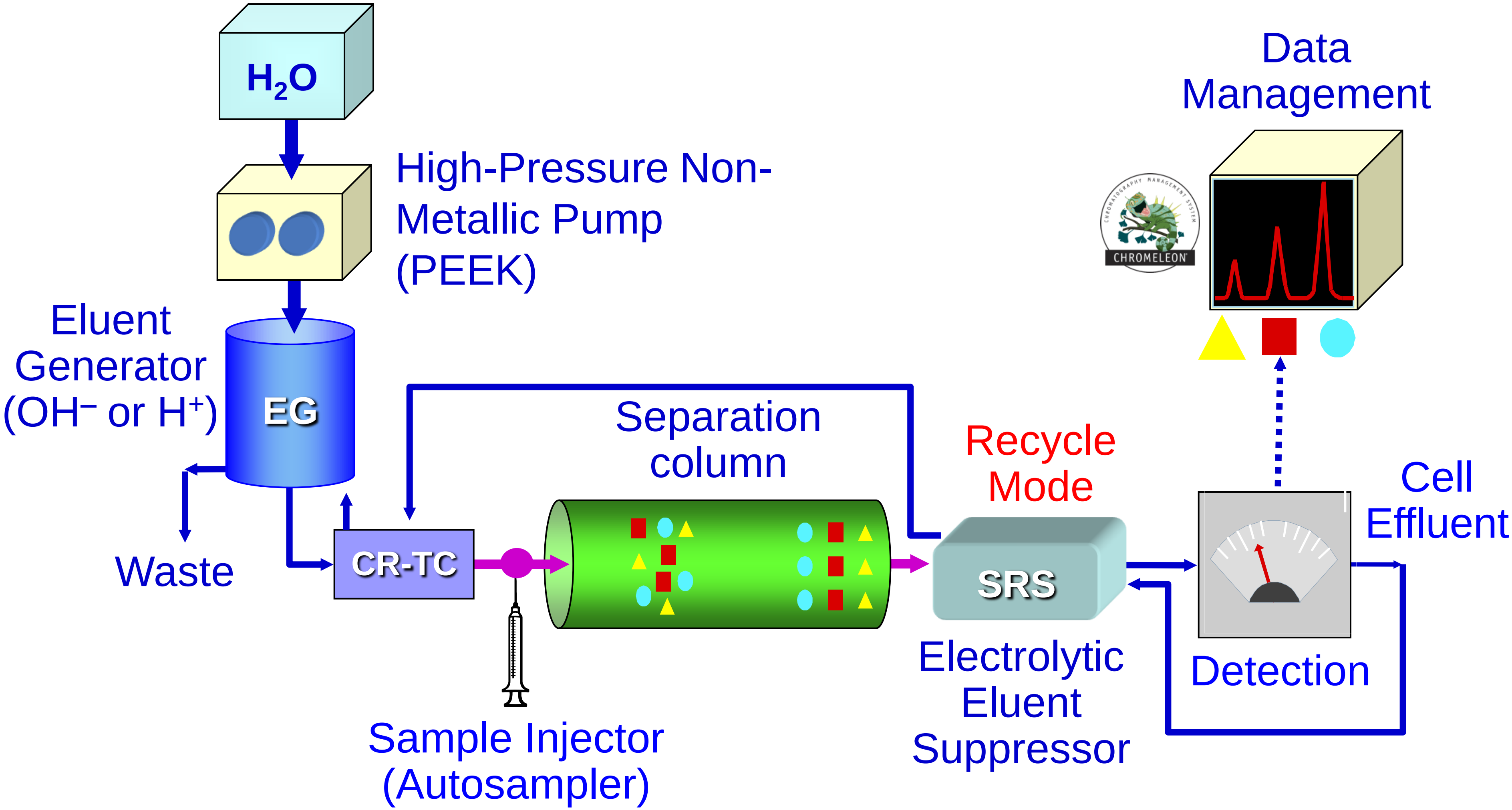
Column:	IonPac CS12A, 4 × 250 mm
Eluent:	20 mM methanesulfonic acid
Flow Rate:	1.0 mL/min
Inj. Volume:	25 µL
Detection:	Suppressed conductivity

Peak:
1. Sodium
2. Ammonium
3. Potassium
4. Magnesium
5. Calcium

Hydroxide Eluent Generation for Anion Analysis



A State of the art Ion Chromatography System



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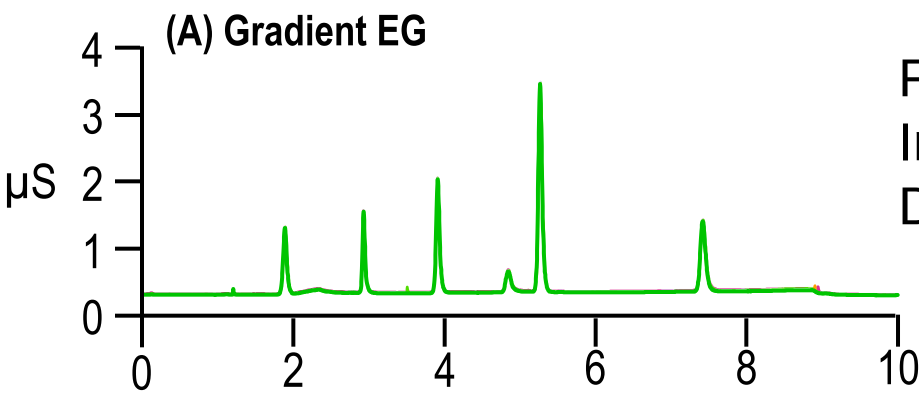
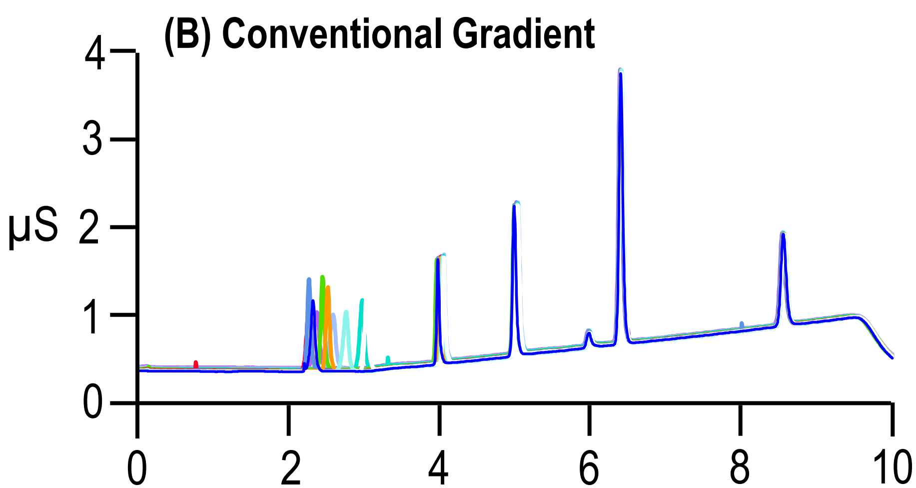
Improved Performance for Anion Gradient Separation

Overlay of 10 Consecutive Runs





Column: IonPac® AG11, AS11, 4 mm
Eluent: 0.5 to 25 mmol/L KOH
From: EG or 0.1 mol/L KOH

Flow Rate: 2 mL/min
Injection: 25 µL
Detection: Conductivity after ASRS® Suppression, recycle mode

Peaks:		
	1. Fluoride	0.2 mg/L
	2. Chloride	0.3
	3. Nitrate	1.0
	4. Sulfate	1.5
	5. Phosphate	1.5

Purity and consistency of Electronically Generated Eluents

High-Resolution Anion Analysis with Eluent Generation

Column: IonPac® AG19, AS19, 4 x 250 mm

Eluent : Potassium hydroxide: 10 mM from 0 to 10 min, 10–58 mM from 10 to 40 min

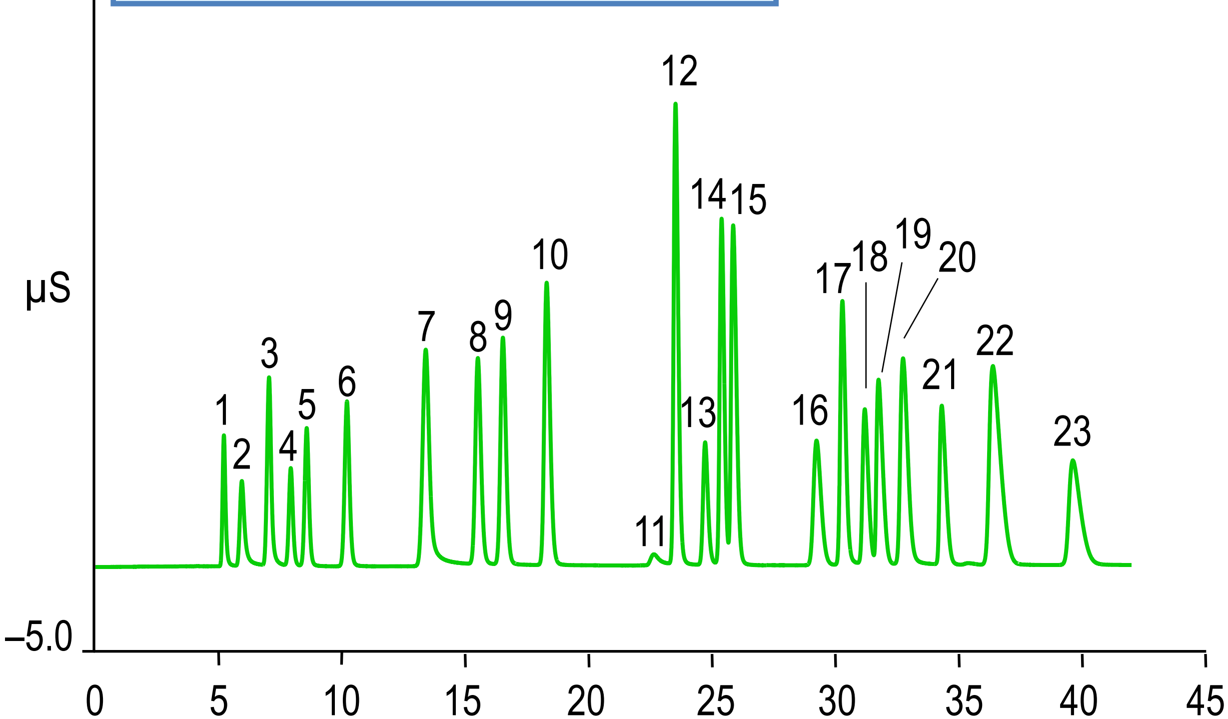
Eluent Source: EGC II KOH cartridge with CR-ATC

Flow Rate: 1.0 mL/min

Temperature: 30 ° C

Suppressor: ASRS® ULTRA II, 4 mm, AutoSuppression® recycle mode, 300 mA

Inj. Volume: 25 µL

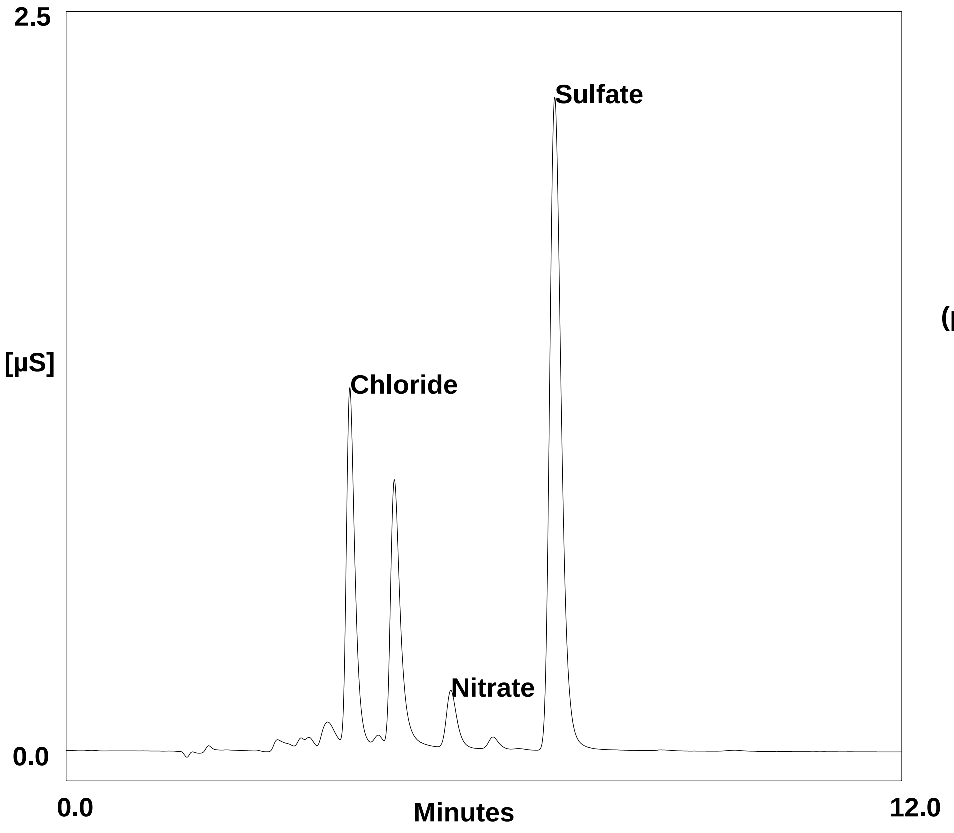


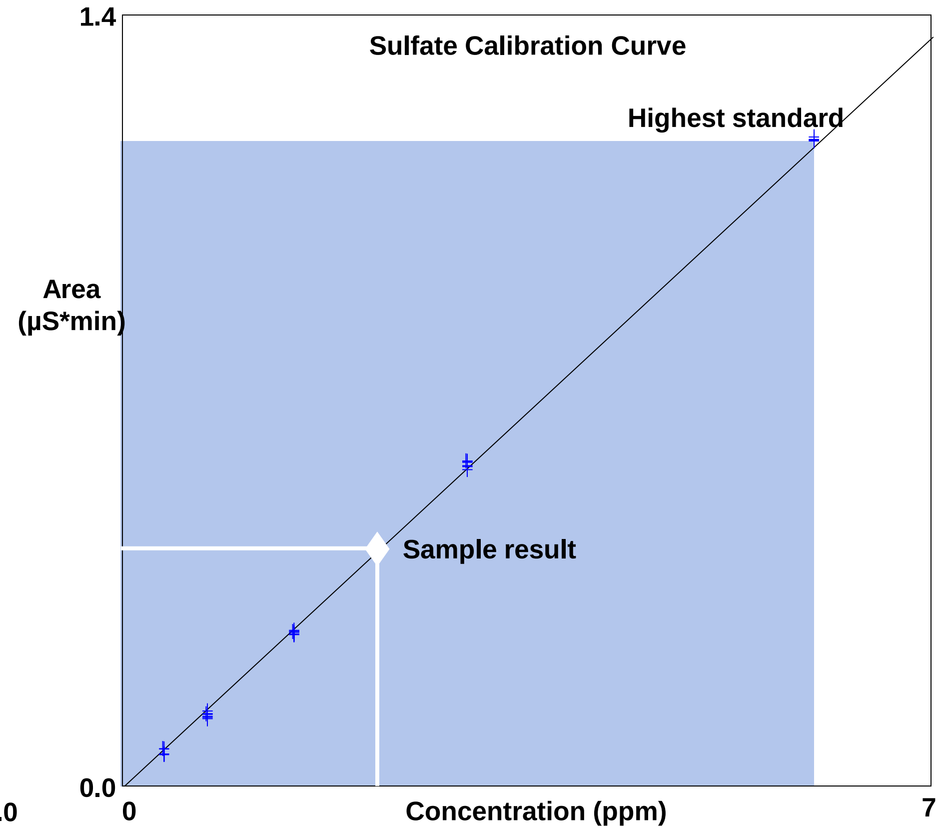
Peaks:

1.	Fluoride	2	mg/L (ppm)
2.	Acetate	10	
3.	Formate	10	
4.	Chlorite	10	
5.	Bromate	20	
6.	Chloride	6	
7.	Nitrite	15	
8.	Chlorate	25	
9.	Bromide	25	
10.	Nitrate	25	
11.	Carbonate	–	
12.	Sulfate	25	
13.	Malonate	25	
14.	Selenate	25	
15.	Oxalate	25	
16.	Iodide	30	
17.	Thiosulfate	25	
18.	Chromate	25	
19.	Phosphate	30	
20.	Fumarate	30	
21.	Arsenate	30	
22.	Thiocyanate	30	
23.	Perchlorate	30	

Linearity of Sulfate with KOH Eluents

Waste sample
AS18 4 mm, 33 mM KOH





Fast, High Resolution Ion Chromatography

- Requirements
  - Fast, High Resolution Columns – Monoliths, small particle sizes
  - Low dead volume inert systems capable of higher pressures
  - Higher flow rates
  - Capillary systems

WHY?

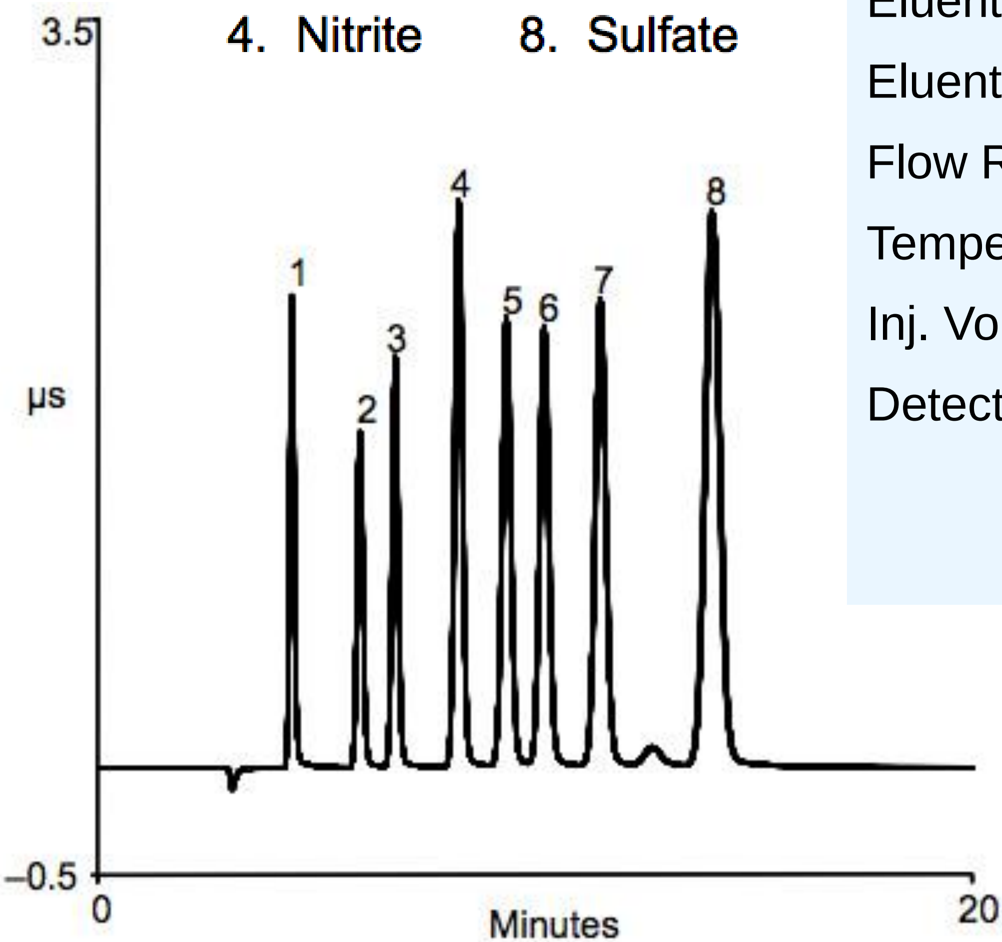
- Faster more frequent analysis
- More information from the sample as resolution increases
- Always running and available for analysis
- Ease of use

Typical Conventional and Capillary IC Operating Parameters

	Conventional IC	Capillary IC
Column i.d.	4 mm	0.40 mm
Flow Rate	1.0 mL/min	10 µL/min
Injection Loop	25 µL	0.4 µL
Suppressor Dead Volume	60 µL	0.6 µL
EG Current (50 mM KOH)	80.4 mA	0.804 mA
K+ Consumption/Year	26.3 Moles (50 mM KOH)	0.263 Moles (50 mM KOH)
H_2O Consumption/Year	525.6 L	5.256 L

Separation of Common Anions using a Capillary AS19 Column – Can Capillary flow be reproducible

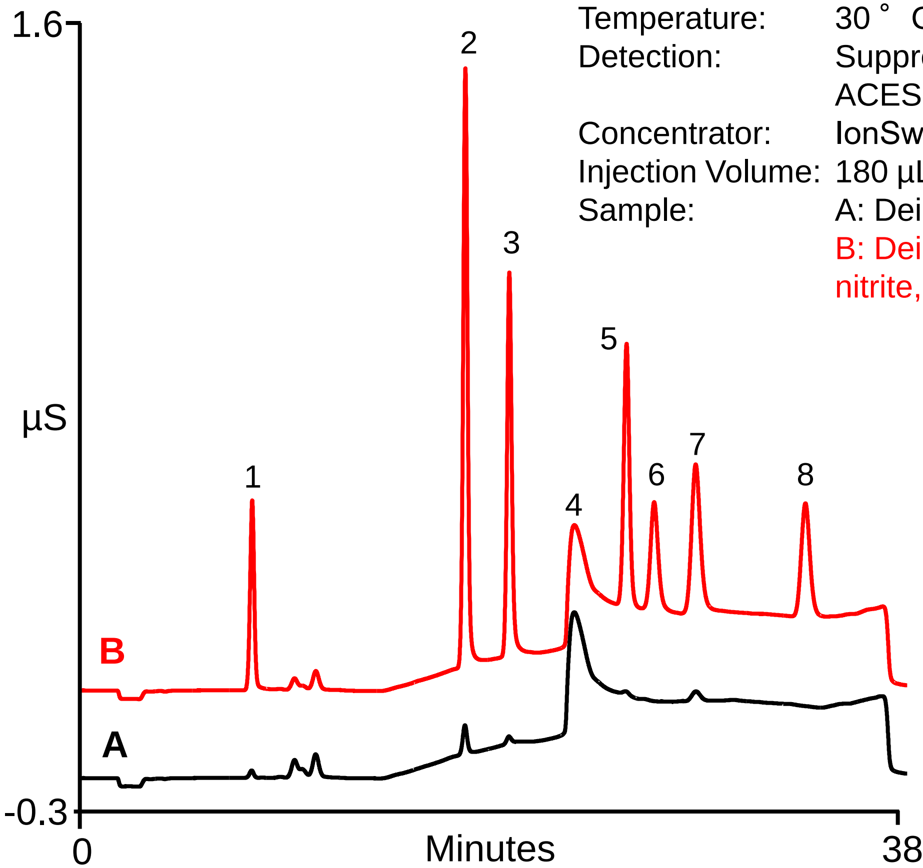
Peaks:
1. Fluoride
2. Bromate
3. Chloride
4. Nitrite
5. Chlorate
6. Bromide
7. Nitrate
8. Sulfate



Column:	IonPac® AS19 column (0.4 mm × 25 cm)
Eluent Source:	Capillary EGC-KOH cartridge
Eluent:	20 mM KOH
Flow Rate:	10 µL/min
Temperature:	30 ° C
Inj. Volume:	0.4 µL
Detection:	Suppressed conductivity with ACES™ 300, AutoSuppression® recycle mode

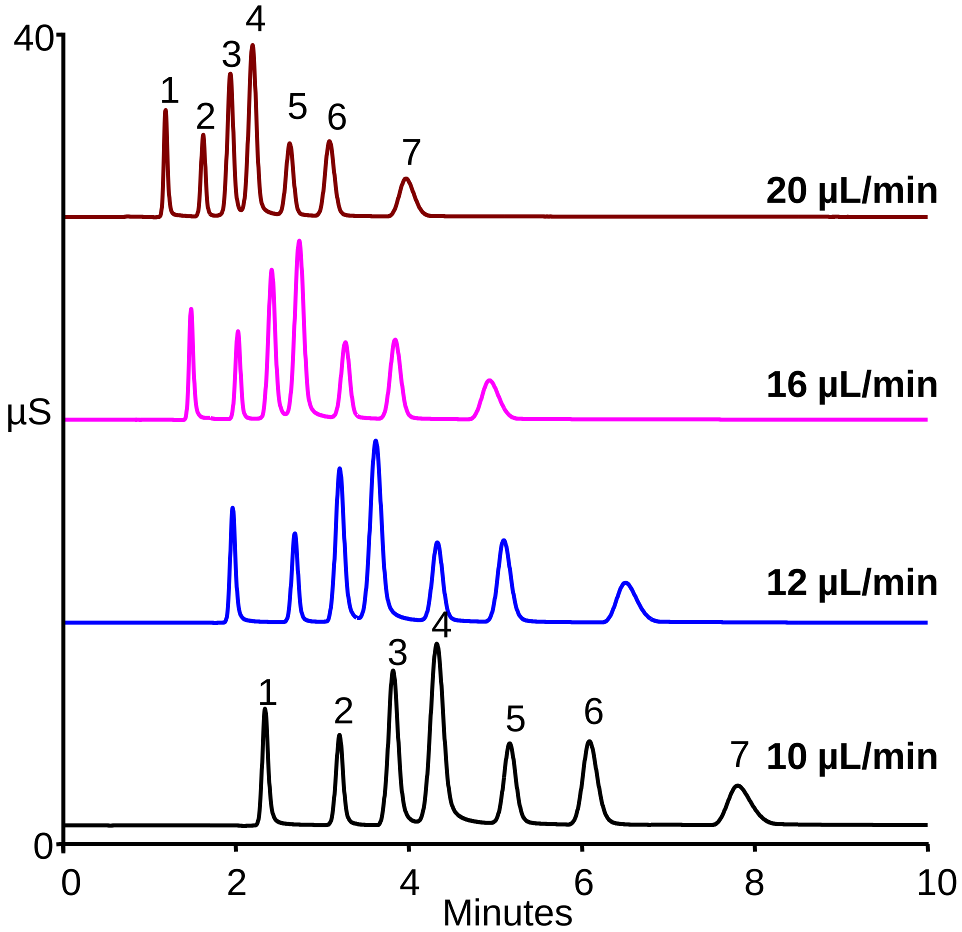
Trace Level Anion Analysis on a Capillary Column with only 180µl injected

Column:	IonPac® AS15 column (0.4 × 250 mm)
Eluent Source:	EGC-KOH capillary cartridge
Eluent:	7 mM KOH (0 to 10 minutes), 7 to 32 mM KOH (10 to 16 minutes), 32 to 50 mM KOH (16 to 30 minutes), 50 to 65 mM (30 to 33 minutes), 7 mM KOH (33 to 38 minutes)
Flow Rate:	12 µL/min
Temperature:	30 ° C
Detection:	Suppressed conductivity, Anion Capillary Electrolytic Suppressor, ACES™ 300, AutoSuppression recycle mode
Concentrator:	IonSwift™ MAC-100 Concentrator (0.5 mm × 80 mm)
Injection Volume:	180 µL
Sample:	A: Deionized water
	B: Deionized water spiked with 0.5 µg/L Fluoride, 2.5 µg/L chloride, nitrite, bromide, nitrate, and phosphate, 5.0 µg/L sulfate



Peak	A	B
1. Fluoride	0.018	0.48 µg/L
2. Chloride	0.12	2.49
3. Nitrite	0.042	2.53
4. Carbonate	–	–
5. Sulfate	0.075	4.72
6. Bromide	–	2.36
7. Nitrate	0.15	2.58
8. Phosphate	–	2.15

Fast IC Inorganic Capillary Anion Analysis at Different Flow Rates



Column: IonPac® AS18-Fast column (0.4 mm × 15 cm)

Eluent Source: Capillary EGC-KOH cartridge

Eluent: 33 mM KOH

Flow Rate: 10 to 20 µL/min

Temperature: 30 ° C

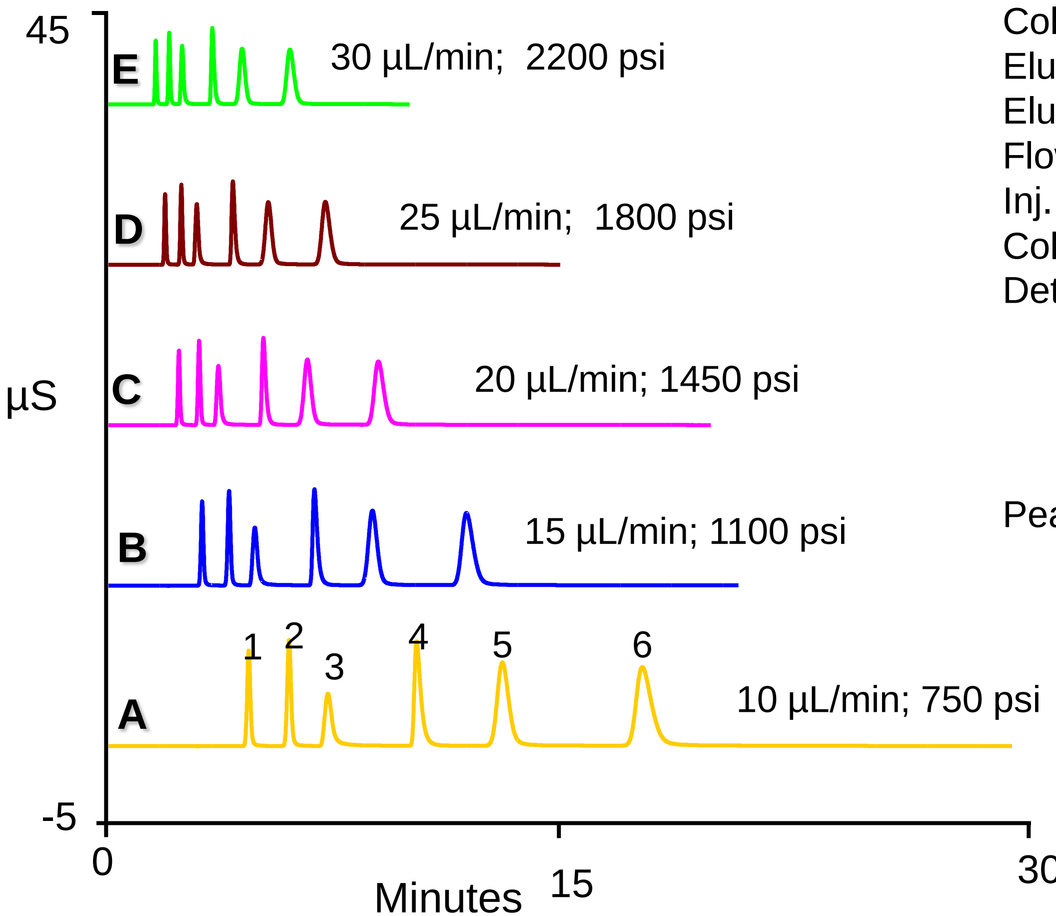
Detection: Suppressed conductivity with ACES™ 300, AutoSuppression® recycle mode

Inj. Volume: 0.4 µL

Peaks:

	Retention Time at 20 µL/min (min)	Concentration (mg/L)
1. Fluoride	1.187	1.0
2. Chloride	1.623	1.5
3. Nitrite	1.937	5.0
4. Sulfate	2.197	7.5
5. Bromide	2.623	5.0
6. Nitrate	3.083	5.0
7. Phosphate	3.983	7.5

Fast IC: Inorganic Capillary Cation analysis at Different Flow Rates



Column:	IonPac® CS16, 0.5 mm
Eluent Source:	EGC-MSA Capillary Cartridge
Eluent:	30 mM MSA
Flow Rate:	See Chromatogram
Inj. Volume:	0.4 µL
Column Temp.:	40 ° C
Detection:	Suppressed Conductivity, Cation Capillary Electrolytic Suppressor, CCES™ 300 AutoSuppression recycle mode

Peaks:		
1. Lithium	0.5	mg/L
2. Sodium	2.0	
3. Ammonium	2.5	
4. Potassium	5.0	
5. Magnesium	2.5	
6. Calcium	5.0	

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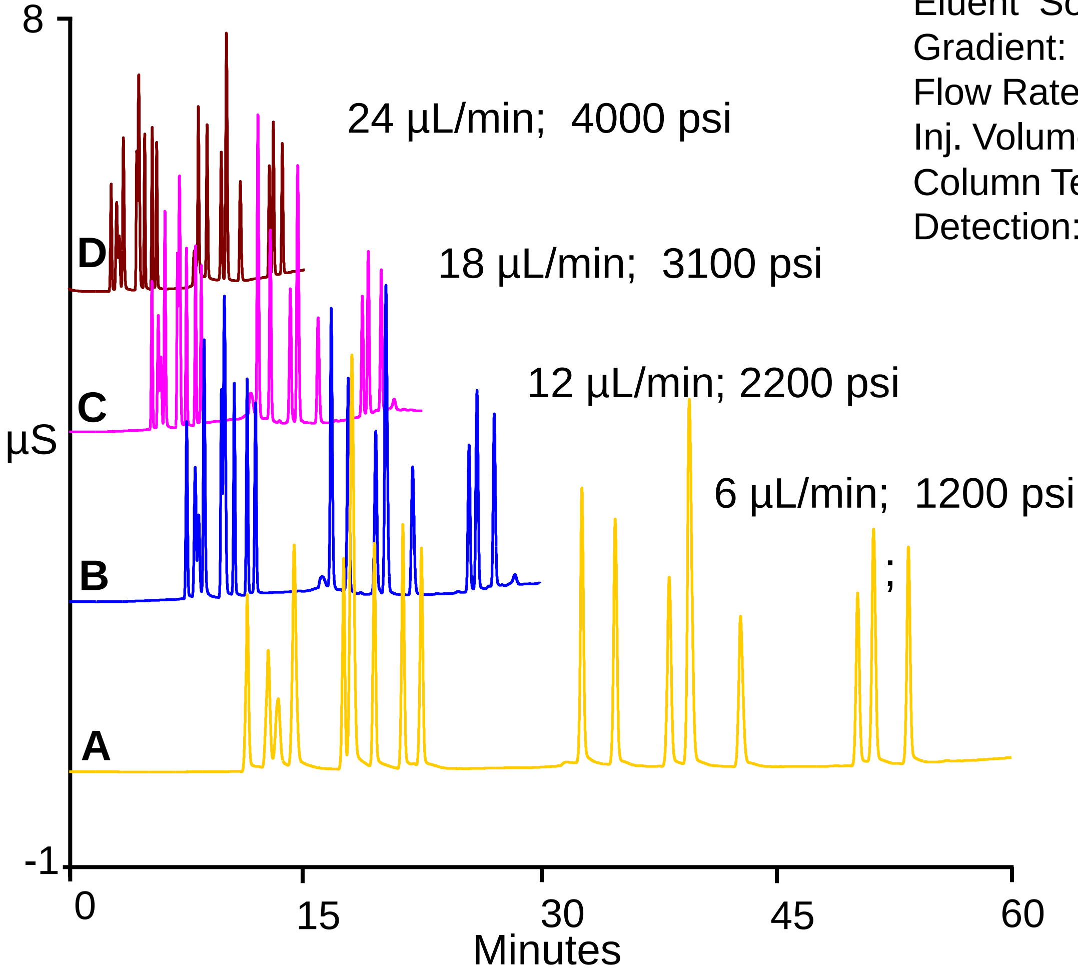
Fast IC: Inorganic Capillary Cation analysis at Different Flow Rates



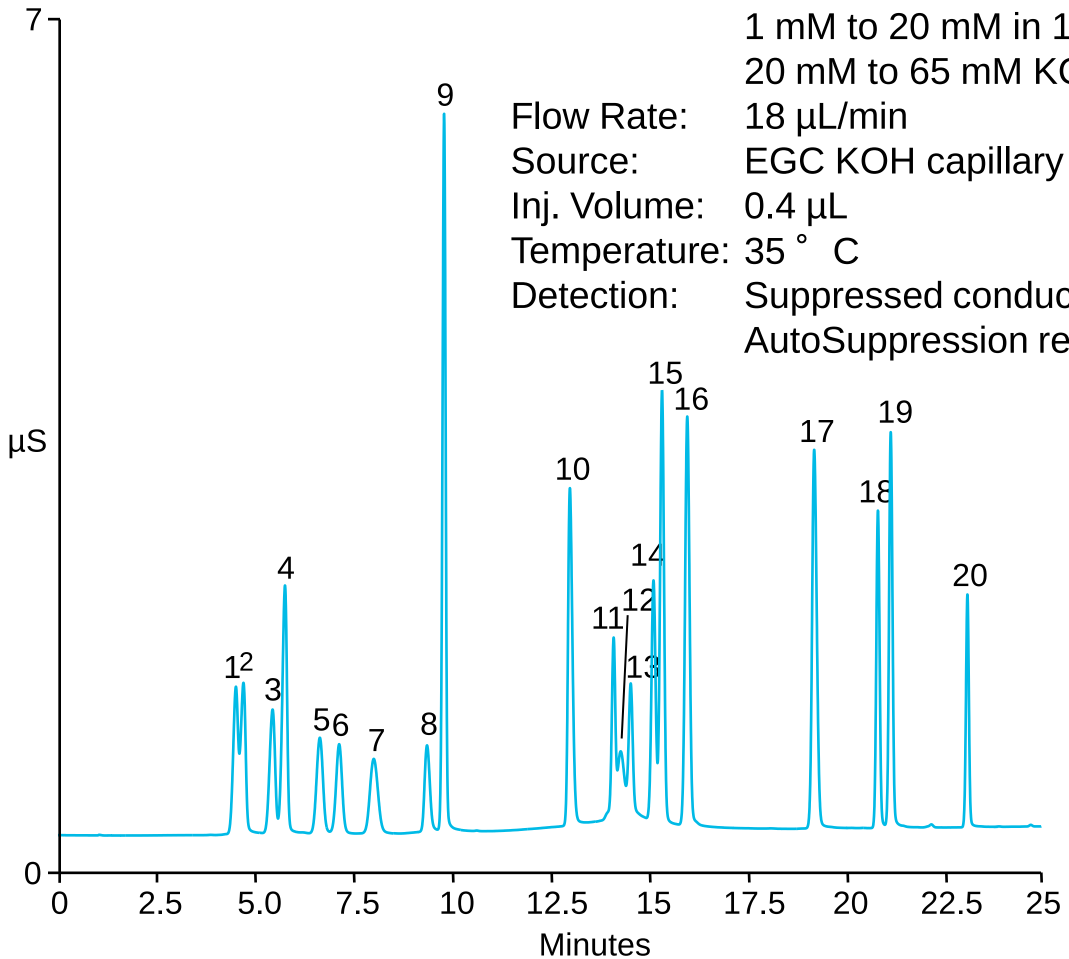
Column:	IonSwift® MAX-200, 0.25 mm
Eluent Source:	EGC-KOH capillary cartridge
Gradient:	KOH gradient from 2 mM to 50 mM
Flow Rate:	See Chromatogram
Inj. Volume:	0.4 µL
Column Temp.:	30 ° C
Detection:	Suppressed Conductivity, Anion Capillary Electrolytic Suppressor, ACES™ 300, AutoSuppression recycle mode

Peaks:

1. Fluoride
2. Acetate
3. Formate
4. Butyrate
5. Galacturonate
6. Chloride
7. Nitrite
8. Bromide
9. Nitrate
10. Carbonate
11. Sulfate
12. Oxalate
13. Tungstate
14. Phosphate
15. Chromate
16. Citrate
17. Isocitrate
18. cis-Aconitate
19. trans-Aconitate

Fermentation Broth Organic and Inorganic Anions Using a monolithic 0.25 × 250 mm Column

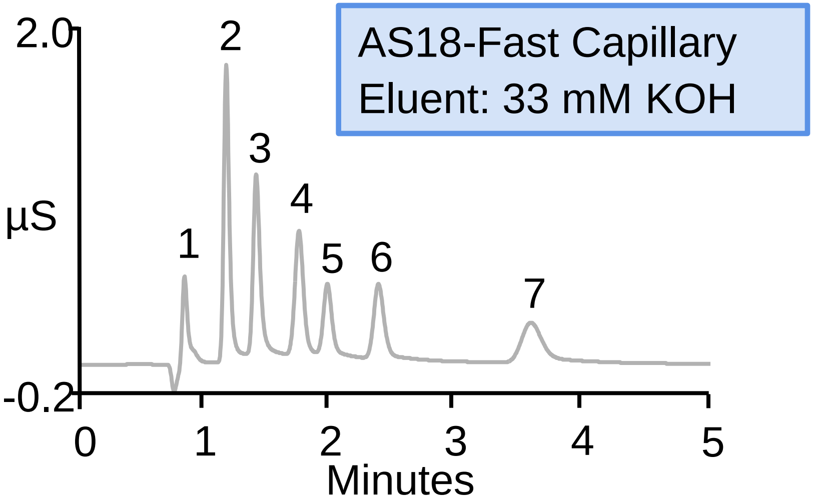
Column:	IonSwift MAX-100G, MAX-100 capillary column
Eluent:	0.1 mM to 1 mM KOH in 7 min, 1 mM to 20 mM in 10 min, 20 mM to 65 mM KOH in 7 min
Flow Rate:	18 µL/min
Source:	EGC KOH capillary
Inj. Volume:	0.4 µL
Temperature:	35 ° C
Detection:	Suppressed conductivity, ACES 300, AutoSuppression recycle mode



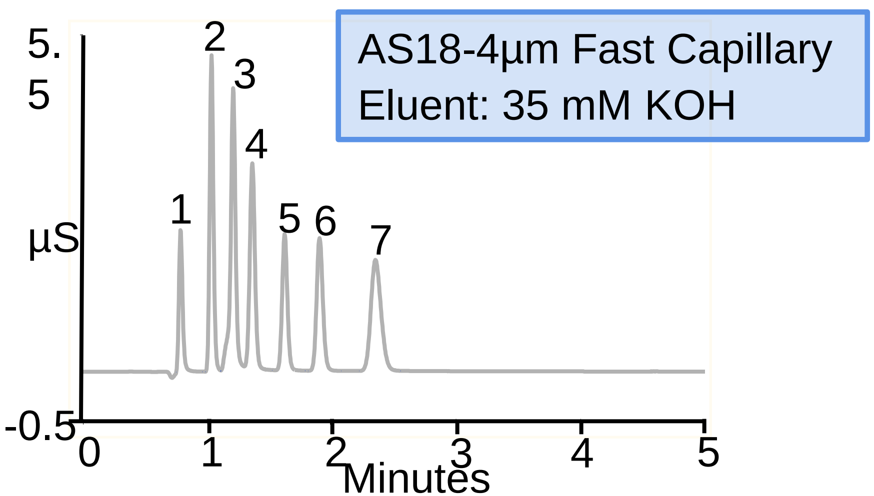
Peaks:

1. Lactate	2 mg/L
2. Acetate	2
3. Propionate	2
4. Formate	2
5. Butyrate	2
6. Pyruvate	2
7. Isovalerate	2
8. Valerate	2
9. Chloride	2
10. Nitrate	2
11. Malate	2
12. Carbonate	–
13. Malonate	2
14. Maleate	2
15. Sulfate	2
16. Oxalate	2
17. Phosphate	4
18. Citrate	4
19. Isocitrate	4
20. Pyrophosphate	4

4µm Particle Size Fast Capillary Columns



Column: See chromatogram
Eluent: See chromatogram
Eluent Source: EGC-KOH capillary cartridge
Temperature: 30 ° C
Flow Rate: 30 µL/min
Inj. Volume: 0.4 µL
Detection: Suppressed conductivity, Anion Capillary Electrolytic Suppressor (ACES™ 300) AutoSuppression® recycle mode



Peaks:			
	1. Fluoride	0.2	mg/L
	2. Chloride	0.5	
	3. Nitrite	1.0	
	4. Sulfate	1.0	
	5. Bromide	1.0	
	6. Nitrate	1.0	
	7. Phosphate	2.0	

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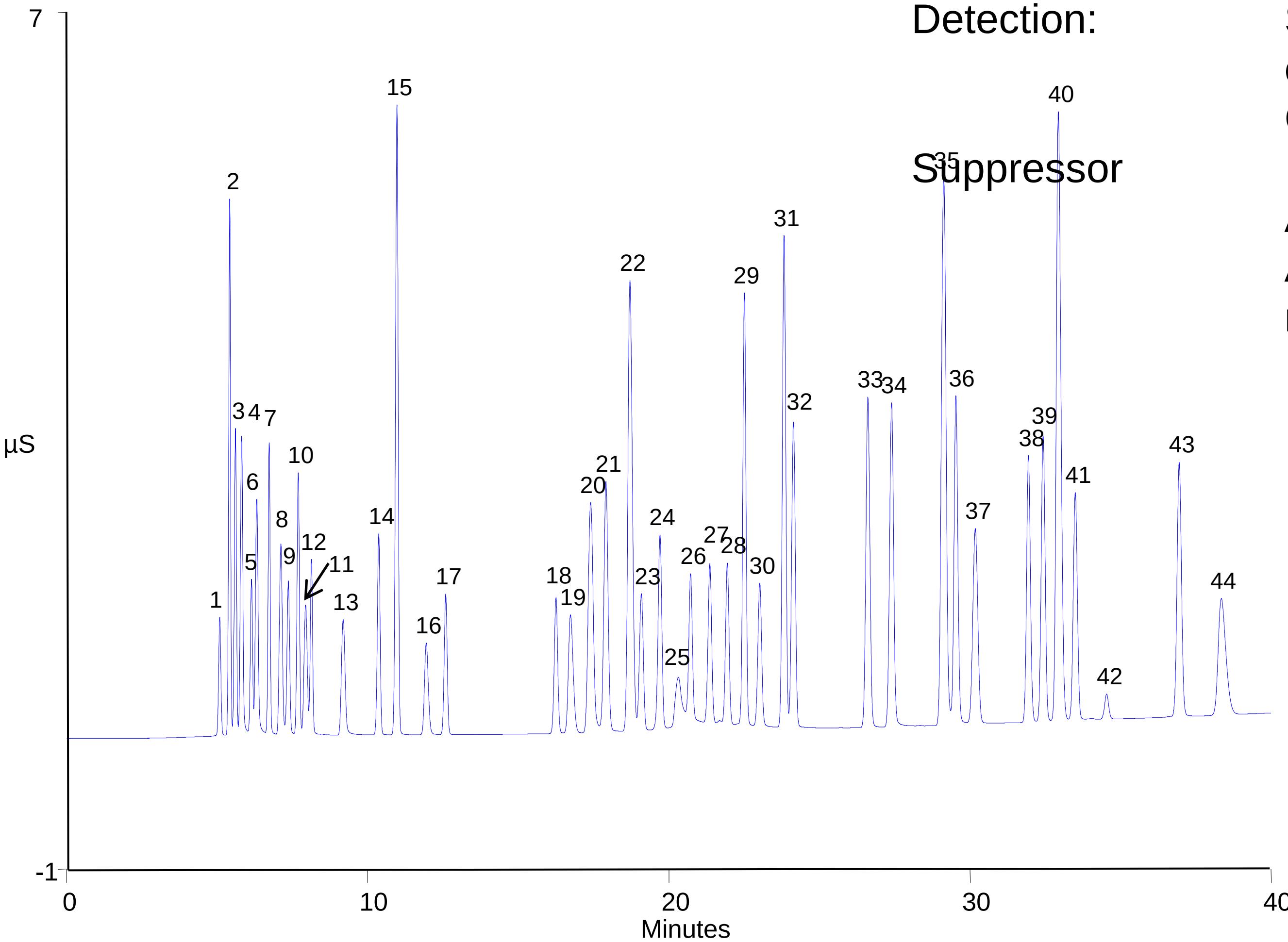
4µm Particle Size High Resolution Columns

Column: IonPac AS11-HC-4µm HR, capillary column
Eluent: 1-14 mM KOH in 16 min, 14-55 mM KOH in 24 min,

Eluent Source: EGC KOH capillary cartridge
Flow Rate: 15 µL/min
Inj. Volume: 0.4 µL
Temperature: 30 ˚C
Detection: Suppressed conductivity, Anion Capillary Electrolytic Suppressor

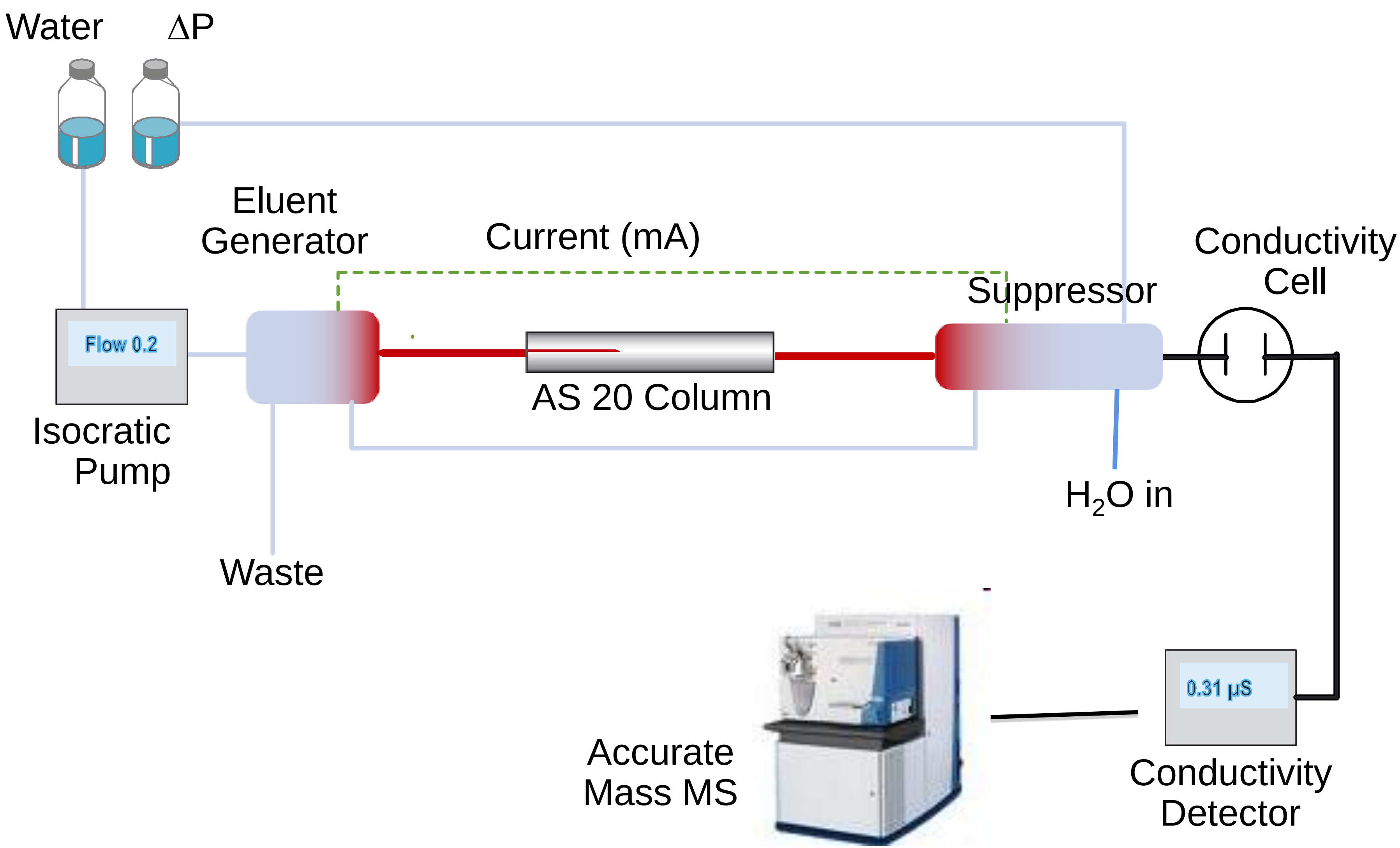
ACES™ 300, 24 mA AutoSuppression recycle mode



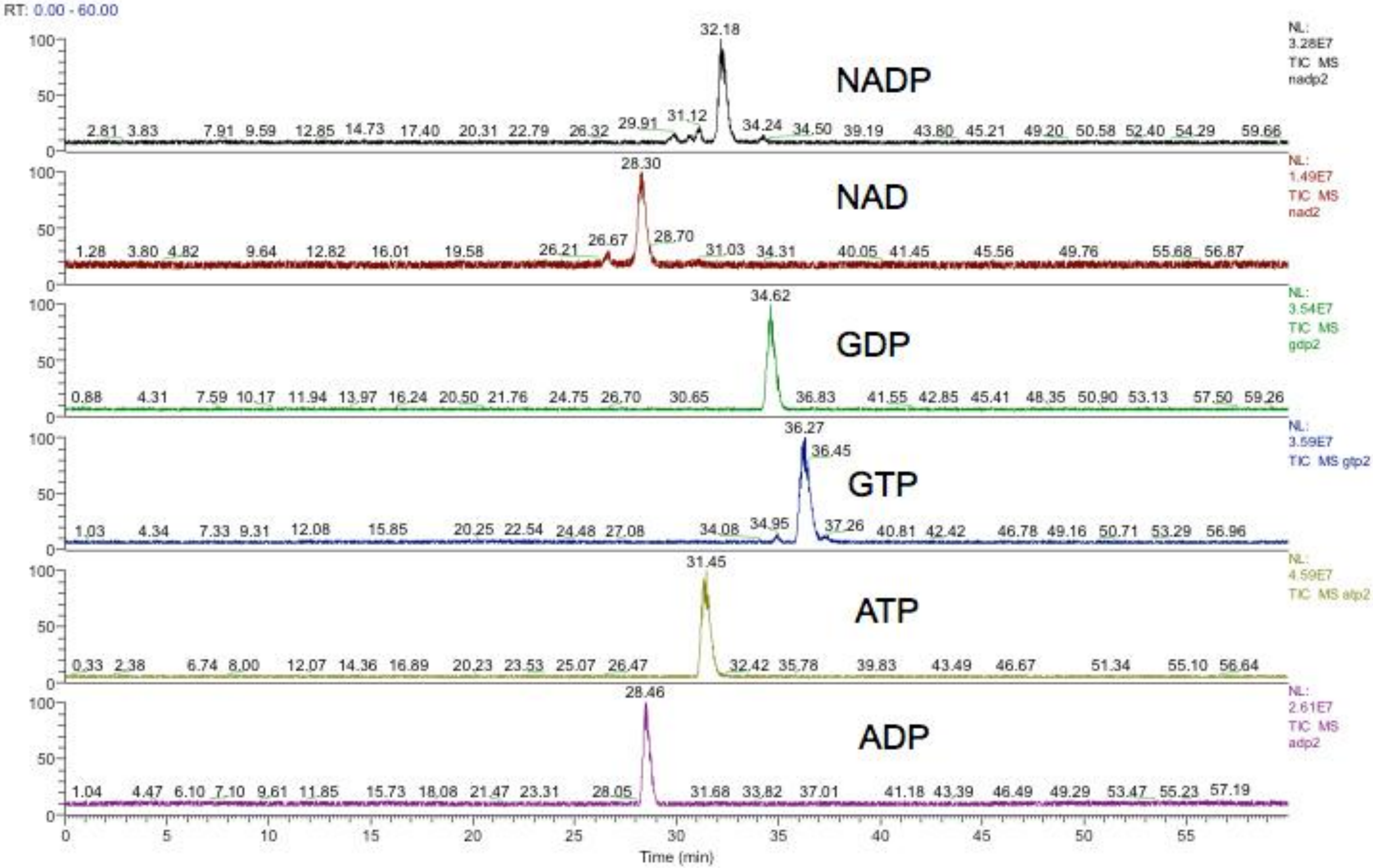
IC-MS

- MS compatible Ion Exchange
  - Continuous Suppression IC system
- Electrolytic gradient generation
  - isocratic deionised water used from the pump
  - gradient generated pre-column electrolytically
- Electrolytic suppression
  - Exchange of post-column K^+ with H_3O^+ using electronic suppressor

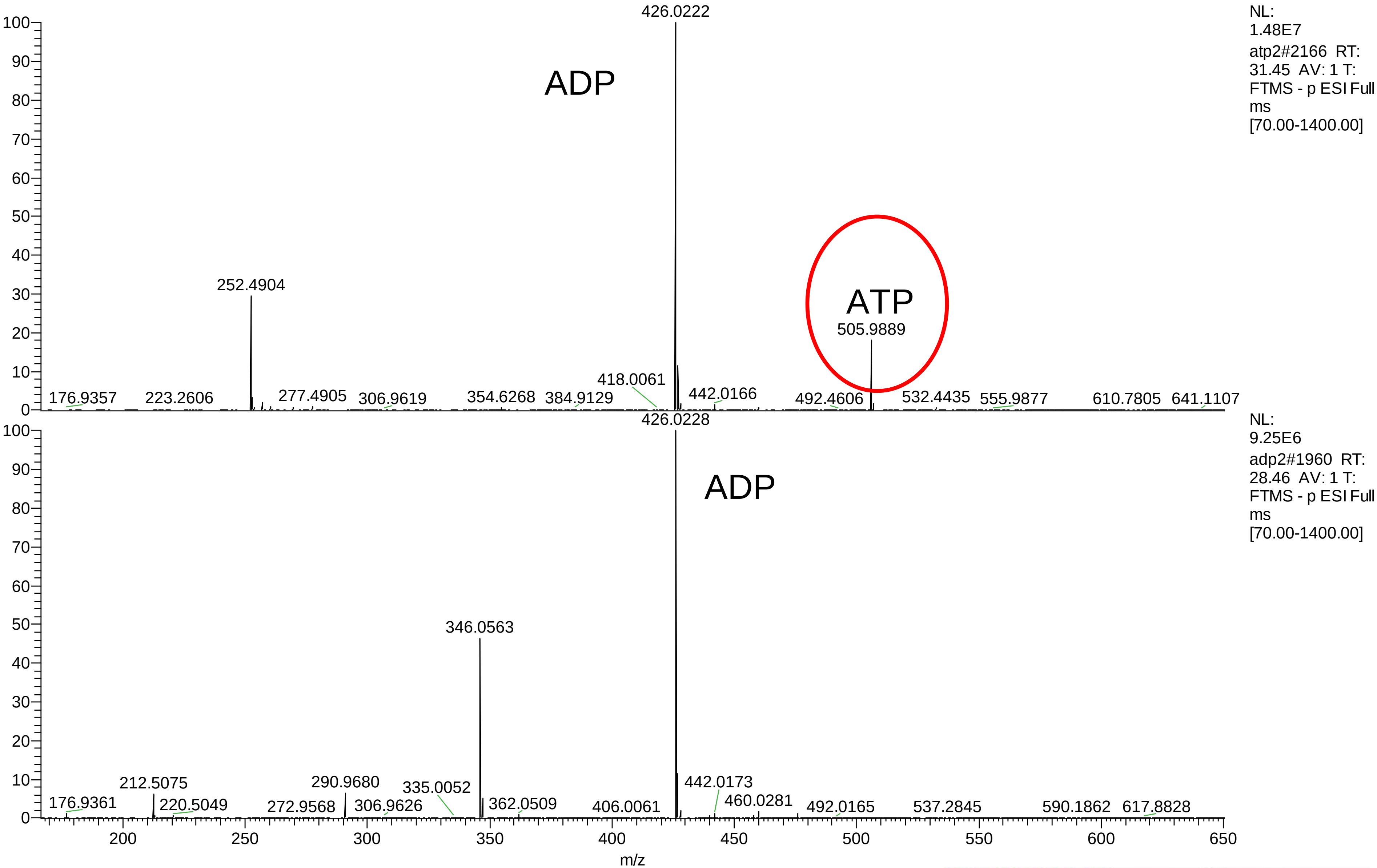
IC-MS Schematics



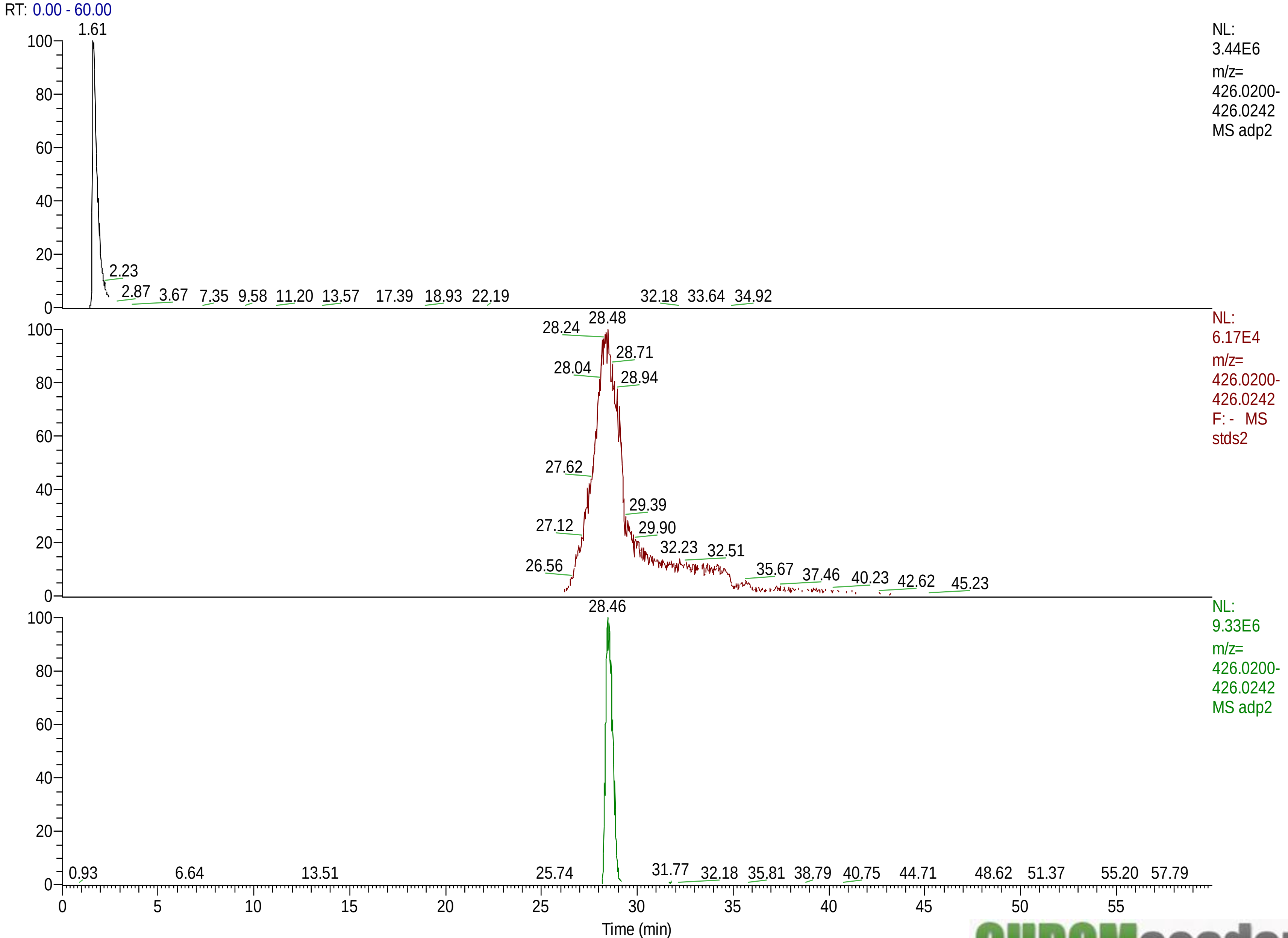
IC separation of key metabolites that run poorly or not at all on HILIC



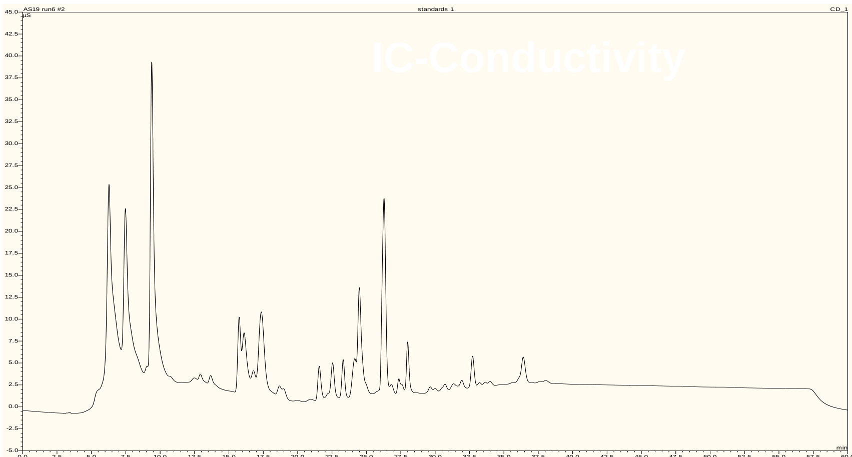
Ambiguity of identification due to fragmentation is common

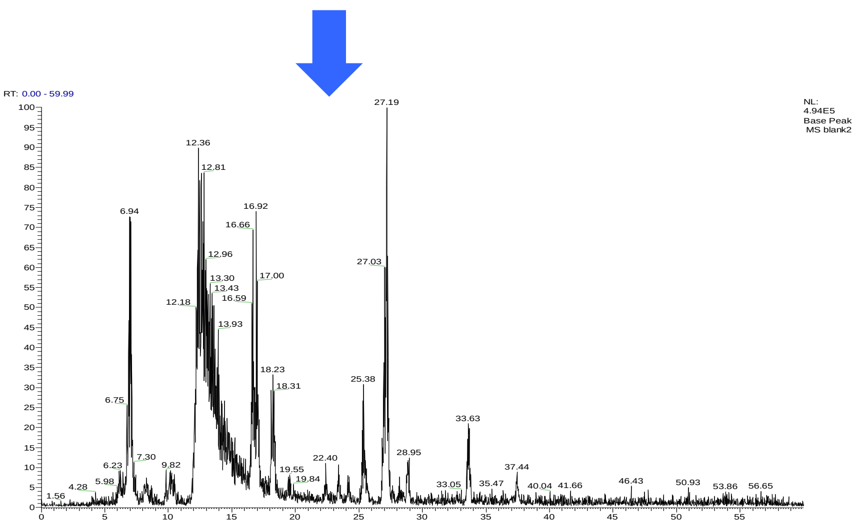


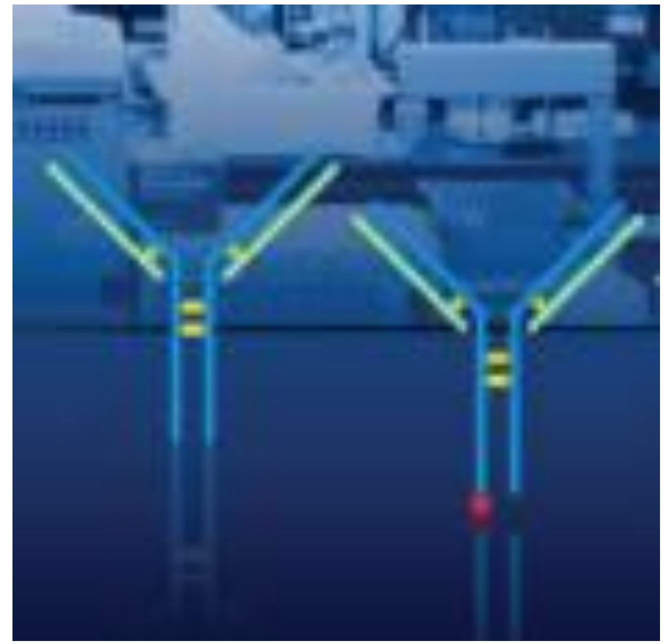
ADP on 3 different stationary phases



Metabolomics Solution for charged intermediates – Capillary IC-MS







University Professor:

"IC separates what is in the void volume of HPLC"

Summary

- **Wide range of IC Columns:**
  - Capacity, Selectivity, Specific applications
- **Suppression is the Key to Analytical Ion Chromatography**
  - Continuous Electrolytic Suppression allows the use of gradients and high capacity columns.
  - Robust, reproducible, quantitative and simple to use
- **Capillary IC a very powerful and easy to use analytical technique**
  - Always On/Always Ready, Ease of use, Fast with High Resolution
  - **ICMS – Ultimate in High Performance, Extreme Flexibility and Information Rich for Method Development and Complex Samples**

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